Bretherick's

Handbook of Reactive Chemical Hazards

VOLUME 1

7th EDITION

Edited by P G Urben

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Bretherick's
Handbook of
Reactive Chemical Hazards

Seventh Edition

Volume 1

AN INDEXED GUIDE TO PUBLISHED DATA

Bretherick's Handbook of
Reactive Chemical Hazards

Seventh Edition — Volume 1

Edited by
P G Urben

Assisted by
M J Pitt
Department of Chemical and Process Engineering
University of Sheffield

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Preface to the Seventh Edition

It is a regret, to the Editor, his assistants, and surely to readers, that Leslie Bretherick died in April 2003 after a short period of overt illness. This work is his major memorial. The measure of how well he wrought is that, in this third edition after his declining sight caused him to hand over the reins, he is still responsible for the initial selection of more than 70% of compound and group entries, however much these may subsequently have been augmented. Only three 'new' compounds have entered this edition on hazard reports from literature which he might have found, but did not, in the days before computers, keywords and hazard warnings in bold or italic, made winnowing the literature as easy as it is today.

The general lines and layout of his *maximum opus* remain little changed.

There is a proliferating literature of what is best described as theoretical chemical safety. Leslie Bretherick initially tried to cover all of this but, well before his death, we agreed that Bretherick should concentrate upon the unfortunate incidents that actually occurred, using, we hoped, well-chosen words. Even here, some selection is involved; azides and organic or organometallic perchlorates only gain individual entries if they are either exceptionally sensitive, or advanced as synthetic reagents. Neither do novel compounds proposed as explosives automatically gain entry; they usually have the characteristics of two or more group entries. The theoretical side is not ignored but selectively, and not exhaustively, covered.

The manufacturer's safety data sheets now supplied alongside chemicals, even by laboratory supply houses, are steadily improving and so render reference to published compound safety datasheet compilations otiose. Since many of the recent latter appear to result from cut and paste by uncritical Information Technology specialists, lacking hands-on experience of the chemicals involved, that is perhaps as well.

Internal reorganisation within Reed International means that the Handbook is now published by Elsevier, not Butterworth Heinemann. Thanks are therefore due to the staff of both organisations. Dr Martin Pitt of the University of Sheffield ably assists me in the more purely chemical engineering matters and also in surfing the Internet, whence my criteria for inclusion remain two of these three: I find the report credible, the source is authoritative and the hazard is not already listed. The libraries of the universities of Durham, Edinburgh, and Warwick have helped me to study sources, and thanks are due to my erstwhile employer, become part of Akzo Nobel, for continuing to allow me occasional days off to undertake the work.

The computerised systems of compilation and structure drawing have been changed and I hope that this has not introduced too many unfound flaws and errors. For these, as others, I must take responsibility and I hope that readers will be unsparing in pointing them out.

But, reader, the ultimate responsibility for your safety remains with you: study, think, and experiment with caution while doubt remains. And, should you thus find new hazard, please report it.

P. G. URBEN

July 2005

Preface to the First Edition

Although I had been aware during most of my career as a preparative chemist of a general lack of information relevant to the reactive hazards associated with the use of chemicals, the realisation that this book needed to be compiled came soon after my reading *Chemistry & Industry* for June 6th, 1964. This issue contained an account of an unexpected laboratory explosion involving chromium trioxide and acetic anhydride, a combination which I knew to be extremely hazardous from close personal experience 16 years previously.

This hazard had received wide publicity in the same journal in 1948, but during the intervening years had apparently lapsed into relative obscurity. It was then clear that currently existing arrangements for communicating 'well-known' reactive chemical hazards to practising chemists and students were largely inadequate. I resolved to try to meet this obvious need for a single source of information with a logically arranged compilation of available material. After a preliminary assessment of the overall problems involved, work began in late 1964.

By late 1971, so much information had been uncovered but remained to be processed that it was apparent that the compilation would never be finished on the spare-time basis then being used. Fortunately I then gained the support of my employers, the British Petroleum Company, Ltd., and have now been able to complete this compilation as a supporting research objective since January 1972.

The detailed form of presentation adopted has evolved steadily since 1964 to meet the dual needs for information on reactive chemical hazards in both specific and general terms, and the conflicting practical requirements of completeness and brevity. A comprehensive explanation of how this has been attempted, with suggestions on using this Handbook to best advantage, is given in the Introduction.

In an attempt to widen the scope of this work, unpublished information has been sought from many sources, both by published appeals and correspondence. In this latter area, the contribution made by a friend, the late Mr A. Kruk-Schuster, of Laboratory Chemicals Disposal Company, Ltd., Billericay, has been outstanding. During 1965–1968 his literature work and global letter campaign to 2000 University chemistry departments and industrial institutions yielded some 300 contributions.

The coverage attempted in this Handbook is wide, but is certainly incomplete because of the difficulties in retrieving relevant information from original literature when it does not appear in the indices of either primary or abstract journals. Details of such new material known to users of this Handbook and within the scope given in the Introduction will be welcomed for inclusion in supplementary or revised editions of this work.

L.B

October 1974

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Volume 1

INTRODUCTION

REACTIVE CHEMICAL HAZARDS

SPECIFIC CHEMICALS
(Elements and compounds arranged in formula order)

Introduction

**THIS SHOULD BE READ THROUGH CAREFULLY
TO GAIN FULL BENEFIT FROM WHAT FOLLOWS**

Aims of the Handbook

This compilation has been prepared and revised to give access to a wide and up-to-date selection of documented information to research students, practising chemists, safety officers and others concerned with the safe handling and use of reactive chemicals. This will allow ready assessment of the likely potential for reaction hazards which may be associated with an existing or proposed chemical compound or reaction system.

A secondary, longer-term purpose is to present the information in a way which will, as far as possible, bring out the causes of, and interrelationships between, apparently disconnected facts and incidents. This is designed to encourage an increased awareness of potential chemical reactivity hazards in school, college and university teaching laboratories, and to help to dispel the relative ignorance of such matters which is still in evidence in this important area of safety training during the formative years of technical education.

Others involved in a more general way with the storage, handling, packing, transport and distribution of chemicals, or emergencies related thereto, are likely to find information of relevance to their activities.

Scope and source coverage

This Handbook includes all information which had become available to the Editor by the end of 2004 on the reactivity hazards of individual elements or compounds, either alone or in combination. Appropriate source references are included to give access to more expansive information than that compressed into the necessarily abbreviated text entries.

A wide variety of possible sources of published information has been scanned to ensure maximum coverage. Primary sources have largely been restricted to journals known to favour or specialise in publication of safety matters, and the textbook series specialising in synthetic and preparative procedures.

Secondary sources have been a fairly wide variety of both specialised and general textbooks and encyclopaedic collections (notably those of Mellor, Sidgwick, Pascal and Bailar in the inorganic area, Houben-Weyl in the organic and organometallic areas, and both Kirk-Othmer and Ullmann in the industrial area). Section 50 of *Chemical Abstracts*, the CAS selection *Chemical Hazards, Health, & Safety*, the *Universities' Safety Association Safety News* (now lapsed), the CIA *CISHC Chemical Safety Summary*, (publication of which ceased in 1986 after 56 years), and the IChemE *Loss Prevention Bulletin* have been rich sources, together with the later recent RSC *Laboratory Hazards Bulletin* and *Chemical Hazards in Industry*. Additionally, various safety manuals, compilations, summaries, data sheets and case histories have been used, and fuller details of the sources used are set out in Appendix 1. References in the text to textbooks listed in Appendix 1 are characterised by absence of the author's initials after the surname.

Data taken from the Internet has been included when it fulfills two of the following three criteria: The Editor finds it credible; the source is authoritative; the hazard or incident was not previously included.

Information on toxic hazards has been specifically excluded because it is available elsewhere in many well-ordered and readily usable forms. However it should be remembered that many of the compounds included in this Handbook show high reactivity of one sort or another toward other materials, so may in general terms be expected to be reactive even in brief contact with animal organisms or tissue (including yours), with possible toxic effects, either acute or chronic. Toxicity has, however, been considered when a chemical reaction not forseeable by the average student generates a volatile poison – there is no warning that sulfides and acids generate hydrogen sulfide, frequent cause of fatality though that is, but generation of carbon monoxide by interaction of alkali and dried milk is covered.

No attempt has been made to include details of all flammable or combustible materials capable of burning explosively when mixed with air and ignited, nor of most incidents related to this most frequent cause of accidents, such information again being available elsewhere. However, to focus attention on the potential hazards always associated with the use of flammable and especially highly flammable substances, some 560 gases and liquids with flash points below 25°C and/or autoignition temperature below 225°C have been included in the text, their names prefixed with a dagger. The numerical values of the fire hazard-related properties of flash point, autoignition temperature and explosive (flammability) limits in air where known are given in the tabular Appendix 2. Those elements or compounds which ignite on exposure to air are included in the text, but not in the Table.

General arrangement

The information presented on reactive hazards is of two main types, specific or general, and these types of information have been arranged differently in their respective separate volumes 1 and 2.

Specific information on instability of individual chemical compounds, and on hazardous interactions of elements and/or compounds, is contained in the main formula-based Volume 1 of the Handbook. For an example of an unstable compound, *see* Ethyl perchlorate, p. 361
For an example of a hazardous interaction between 2 compounds,
see Nitric acid: Acetone, p. 1635

or 2 separate examples involving the same compound,
see Nitric acid: Acetone, or: Ethanol, pp. 1635, 1636
and one involving 3 compounds,
see Hydrogen peroxide: Nitric acid, Thiourea, p. 84

General information relating to classes or groups of elements or compounds possessing similar structural or hazardous characteristics is contained in the smaller alphabetically based Volume 2.

See ACYL NITRATES, p. 10
    PYROPHORIC METALS, p. 354

References in the text to these general classes or groups of materials is always in small capitals to differentiate them from references to specific chemicals, the names of which are given in normal roman typeface.

Some individual materials of variable composition (substances) and materials which cannot conveniently be formulated and placed in Volume 1 are also included in this general section.

See BLEACHING POWDER, CELLULOSE NITRATE, pp. 57, 66

Both theoretical and practical hazard topics, some indirectly related to the main theme of this book, are also included.

See DISPOSAL, EXPLOSIBILITY, pp. 110, 131
    GAS CYLINDERS, OXYGEN ENRICHMENT, pp. 150, 307

Several topics which bring together incidents involving a common physical cause or effect but different types of chemicals are now included in Volume 2.

See CATALYTIC IMPURITY INCIDENTS, p. 63
    GAS EVOLUTION INCIDENTS, p. 150

Specific chemical entries (Volume 1)

A single unstable compound of known composition is placed in the main first volume and is located on the basis of its empirical molecular formula expressed in the Hill system used by *Chemical Abstracts* (C and H if present, then all other element symbols alphabetically). The use of this indexing basis permits a compound to be located if its structure can be drawn, irrespective of whether a valid name is known for it. A representation of the structure of each compound is given on the third bold title line while the name of the compound appears as the first bold title line. References to the information source are given, followed by a statement of the observed hazard, with any relevant explanation. Cross-reference to similar compounds, often in a group entry, completes the entry. *See* Trifluoroacetyl nitrite, p. 270

Where two or more elements or compounds are involved in a reactive hazard, and an intermediate or product of reaction is identifiable as being responsible for the hazard, both reacting substances are normally cross-referred to the identified product. The well-known reaction of ammonia and iodine to give explosive nitrogen triodide-ammonia is an example of this type. The two entries

Ammonia: Halogens, p. 1730
Iodine: Ammonia, p. 1794

are referred back to the main entry under the identified material

Nitrogen triiodide-ammonia, p. 1799

No attempt has been made, however, to list all combinations of reactants which can lead to the formation of a particular main entry compound.

In a multi-reactant system where no identification of an unstable product was possible, one of the reactants had to be selected as primary reactant to prepare and index the main entry, with the other material(s) as secondary reactant(s). No strictly logical basis of choice for this is obvious.

However, it emerged during the compilation phase that most two component reaction hazard systems of this type involve a fairly obvious oxidant material as one of the reactants. Where this situation was recognised, the oxidant has normally been selected as primary (indexing) reactant, with the other as secondary reactant, following the colon.

See Potassium permanganate: Acetic acid, etc., p.1811

In the markedly fewer cases where an obvious reducant has been involved as one reactant, that was normally selected as primary reactant.

See Lithium tetrahydroaluminate: 3,5-Dibromocyclopentene, p. 47

In the relatively few cases where neither (or none) of the reactants can be recognised as an oxidant or reducant, the choice was made which appeared to give the more informative main entry text.

See Chloroform: Acetone, etc., p. 163

Where some hazard has been noted during the preparation of a specific compound, but without it being possible to identify a specific cause, an entry for that compound states ‘Preparative hazard’, and back-refers to the reactants involved in the preparation.

See Sulfur dioxide, p. 1948

Occasionally, departures from these considerations have been made where such action appeared advantageous in bringing out a relationship between formally unrelated compounds or hazards. In all multi-component cases, however, the secondary reactants (except air and water) appear as formula entries back-referred to the main entry text, so that the latter is accessible from either primary or secondary reactants.

See Dimethyl sulfoxide: Acyl halides (main entry), p. 381
Acetyl chloride: Dimethyl sulfoxide (back reference), p. 312

Grouping of reactants

There are advantages to be gained in grouping together elements or compounds showing similar structure or reactivity, because this tends to bring out the relationships between structure and activity more clearly than separate treatment. This course has been adopted widely for primary reactants (see next heading), and for secondary reactants where one primary reactant has been involved separately with a large number of secondary materials. Where possible, the latter have been collected together under a suitable general group title indicative of the composition or characteristics of those materials.

See Chlorine: Hydrocarbons, p. 1452
Hydrogen peroxide: Metals, Metal oxides, Metal salts, p. 1705
Hydrogen sulfide: Oxidants, p. 1722

This arrangement means, however, that some practice will be necessary on the user's part in deciding into what group an individual secondary reactant falls before the longer-term advantages of the groupings become apparent. The formal group titles listed in Appendix 5, and classified in Appendix 6, will be of use in this connection. However, it should be noted that sometimes informal group titles are used which do not appear in these Appendices.

General group entries (Volume 2)

In some cases literature references relating to well-defined groups of hazardous compounds or to hazard topics have been found, and these are given, with a condensed version of relevant information at the beginning of the topic or group entry, under a suitable bold title, the latter being arranged in alphabetical order in Volume 2.

Cross references to related group or sub-group entries are also included, with a group list of the names and serial (not page) numbers of the chemicals appearing in Volume 1 which lie within the structural or functional scope of the group entry title. Compounds which are closely similar to, but not in strict conformity with, the group definition are indicated by a prefixed asterisk.

The group entries thus serve as sub-indexes for each structurally based group of hazardous compounds. Conversely, each individual compound entry is back-referred to the group entry, and thence to all its strict structural analogues and related congeners included in Volume 1 of this Handbook. Note that these group lists of chemicals are now in alphabetical (not formula) order, and give the serial number (not page number) for the chemical.

These features should be useful in attempts to estimate the stability or reactivity of a compound or reaction system which does not appear in this Handbook. The effects on stability or reactivity of changes in the molecular structure to which the destabilising or reactive group(s) is attached are in some cases discussed in the group entry. Otherwise such information may be gained from comparison of the information available from the individual compound entries listed collectively (now in alphabetical order, with serial number) in the group entry.

Care is, however, necessary in extrapolating from the described properties of compounds to others in which the user of this Handbook may be interested. Due allowance must be made for changes in elemental reactivity up or down the columns of the Periodic Table, and for the effects of variation in chain length, branching and point of group-attachment in organic systems. Purity of materials, possible catalytic effects (positive or negative) of impurities, and scale of operations may all have a direct bearing upon a particular reaction rate. These and other related matters are dealt with in more detail in the following Introductory Chapter.

Nomenclature

With the direct encouragement and assistance of the Publishers, an attempt has been made to use chemical names which conform to recent recommendations of IUPAC. While this has not been an essential part of the compilation, because each title name has the corresponding structural and molecular formula adjacent, it seems nonetheless desirable to minimise possible confusion by adopting the unambiguous system of nomenclature presented in the IUPAC publications.

Where the IUPAC name for a compound is very different from a previously used recent trivial name, the latter is included as a synonym in parentheses (and in single quotes where no longer an acceptable name). Generally, retained trivial names have not been used as main entry titles, but they have often been included in the entry texts. Rarely, on the grounds of brevity, names not conforming strictly to IUPAC principles but recommended for chemicals used in industry in BS 2474: 1983 have been used. The prefix *mixo*-, to represent the mixtures of isomers sometimes used as industrial materials, is a case in point.

Some of the rigidly systematic names selected by the Association for Science Education for their nomenclature list in 1985 from the IUPAC possibilities, and some of the systematic indexing names used by *Chemical Abstracts* since 1972, are given as synonyms in the Index of Chemical Names. This should assist those coming into industry and research with a command of those nomenclature systems but who may be unfamiliar with the current variety of names used for chemicals. The inclusion, where possible, of the CAS Registry Number for each title compound should now simplify the clarification of any chemical name or synonym problems, by reference to the Registry Handbook or other CAS source.

In connection with the group titles adopted for the alphabetically ordered Volume 2, it has been necessary in some cases to devise group names (particularly in the inorganic field) to indicate in a very general way the chemical structures involved in various classes, groups or sub-groups of compounds. For this purpose, all elements have been considered either as METALS or NON-METALS, and of the latter, HALOGENS, HYDROGEN, NITROGEN, OXYGEN, and SULFUR were selected as specially important. Group names have then been coined from suitable combinations of these, such as the simple

METAL OXIDES, NON-METAL SULFIDES
N-HALOGEN COMPOUNDS, NON-METAL HYDRIDES
METAL NON-METALLIDES, COMPLEX HYDRIDES

or the more complex

METAL OXOHALOGENATES
AMMINECHROMIUM PEROXOCOMPLEXES
OXOSALTS OF NITROGENOUS BASES
METAL OXONON-METALLATES

Organic group entries are fairly conventional, such as

HALOALKENES
NITROARL COMPOUNDS
DIAZONIUM SALTS

Where necessary, such group names are explained in the appropriate group entry, of which a full listing is given in Appendix 5, and a classified listing in Appendix 6.

Cross reference system

The cross-reference system adopted in this Handbook plays a large part in providing maximum access to, and use of, the rather heterogeneous collection of information herein. The significance of the five types of cross-reference which have been used is as follows.

See . . . refers to a directly related item.

See also . . . refers to an indirectly related item.

See other . . . refers to listed strict analogues of the compound etc.

See related . . . refers to listed related compounds (congeners) or groups not strictly analogous structurally.

See entry . . . points to a or the relevant reference in Volume 2.

CROSS REFERENCES IN CAPITALS REFER TO VOLUME 2

Information content of individual entries

A conscious effort has been made throughout this compilation to exclude much fringe information not directly relevant to the involvement of chemical reactivity in the various incidents or observations, while giving enough detail to allow the reader to judge the relevance or otherwise of the quoted reference(s) to his or her particular reactivity problems or interests.

It must be stressed that this book can do no more than to serve as a guide to much more detailed information available *via* the quoted references. In all but a few cases it cannot relieve the student or chemist of their moral and now legal obligation to themselves and to their co-workers, to equip themselves with the fullest possible information from the technical literature resources which are widely available, *before* attempting any experimental work with materials known, or suspected, to be hazardous or potentially so. It could be impossible for you *after* the event.

THE ABSENCE OF A MATERIAL OR A COMBINATION OF MATERIALS FROM THIS HANDBOOK CANNOT BE TAKEN TO IMPLY THAT NO HAZARD EXISTS. LOOK THEN FOR ANALOGOUS MATERIALS USING THE GROUP ENTRY SYSTEM AND THE INDEXES THERETO.

One aspect which, although it is absent from most entry texts, is nevertheless of vital importance, is that of the potential for damage, injury or death associated with the various materials and reaction systems dealt with in this Handbook.

Though some of the incidents have involved little or no damage (*see* CAN OF BEANS, p. 61), others have involved personal injuries, often of unexpected severity (*see* SODIUM PRESS, p. 380), and material damage is often immense. For example, the incident given under Perchloric acid: Cellulose derivatives, (reference 1, p. 65) involved damage to 116 buildings and a loss approaching 3M dollars at 1947 values. The death-roll associated with reactive chemical hazards has ranged from 1 or 2 (*see* Tetrafluoroethylene: Iodine pentafluoride, p. 1601) to some 600 with 2000 injured in the incident at Oppau in 1921 (*see* Ammonium nitrate, reference 4, p. 1749), and now to several thousand, with more than 100,000 injured, by methyl isocyanate fumes at Bhopal in 1984 (reference 7, p. 288).

This sometimes vast potential for destruction again emphasises the need to gain the maximum of detailed knowledge *before* starting to use an unfamiliar chemical or reaction system.

Reactive Chemical Hazards

This introductory chapter seeks to present an overview of the complex subject of reactive chemical hazards, drawing attention to the underlying principles and to some practical aspects of minimising such hazards. It also serves in some measure to correlate some of the topic entries in the alphabetically arranged Section 2 of the Handbook.

Basics

All chemical reactions implicitly involve energy changes (energy of activation + energy of reaction), for these are the driving force. The majority of reactions liberate energy as heat (occasionally as light or sound) and are termed exothermic. In a minority of reactions, the reaction energy is absorbed into the products, when both the reaction and its products are described as endothermic.

All reactive hazards involve the release of energy in quantities or at rates too high to be absorbed by the immediate environment of the reacting system, and material damage results. The source of the energy may be an exothermic multi-component reaction, or the exothermic decomposition of a single unstable (often endothermic) compound.

All measures to minimise the possibility of occurrence of reactive chemical hazards are therefore directed at controlling the extent and rate of release of energy in a reacting system. In an industrial context, such measures are central to modern chemical engineering practice. Some of the factors which contribute to the possibility of excessive energy release, and appropriate means for their control, are now outlined briefly, with references to examples in the text.

Kinetic factors

The rate of an exothermic chemical reaction determines the rate of energy release, so factors which affect reaction kinetics are important in relation to possible reaction hazards. The effects of proportions and concentrations of reactants upon reaction rate are governed by the Law of Mass Action, and there are many examples where changes in proportion and/or concentration of reagents have transformed an established uneventful procedure into a violent incident. For examples of the effect of increase in proportion,

see 2-Chloronitrobenzene: Ammonia
Sodium 4-nitrophenoxide

For the effect of increase in concentration upon reaction velocity,
see Dimethyl sulfate: Ammonia
Nitrobenzene: Alkali (reference 2)

The effects of catalysts (which effectively reduce the energy of activation), either intentional or unsuspected, is also relevant in this context. Increase in the concentration of a catalyst (normally used at 1-2%) may have a dramatic effect on reaction velocity.

See Trifluoromethanesulfonic acid: Acyl chlorides, etc
2-Nitroanisole: Hydrogen
HYDROGENATION CATALYSTS

The presence of an unsuspected contaminant or catalytic impurity may affect the velocity or change the course of reaction. For several examples,
see CATALYTIC IMPURITY INCIDENTS

In the same context, but in opposite sense, the presence of inhibitors (negative catalysts, increasing energy of activation) may seriously interfere with the smooth progress of a reaction. An inhibitor may initiate an induction period which can lead to problems in establishing and controlling a desired reaction. For further details and examples,
see INDUCTION PERIOD INCIDENTS

Undoubtedly the most important factor affecting reaction rates is that of temperature. It follows from the Arrhenius equation that the rate of reaction will increase exponentially with temperature. Practically, it is found that an increase of 10°C in reaction temperature often doubles or trebles the reaction velocity.

Because most reactions are exothermic, they will tend to accelerate as reaction proceeds unless the available cooling capacity is sufficient to prevent rise in temperature. Note that the exponential temperature effect accelerating the reaction will exceed the (usually) linear effect of falling reactant concentration in decelerating the reaction. When the exotherm is large and cooling capacity is inadequate, the resulting accelerating reaction may proceed to the point of loss of control (runaway), and decomposition, fire or explosion may ensue.

The great majority of incidents described in the text may be attributed to this primary cause of thermal runaway reactions. The scale of the damage produced is related directly to the size, and more particularly to the *rate*, of energy release.
See RUNAWAY REACTIONS

Reactions at high pressure may be exceptionally hazardous owing to the enhanced kinetic energy content of the system.
See HIGH-PRESSURE REACTION TECHNIQUES

Although detailed consideration of explosions is outside the scope of this Handbook, three levels of intensity of explosion (i.e. rates of fast energy release) can be discerned and roughly equated to the material damage potential.

Deflagration involves combustion of a material, usually in presence of air. In a normal liquid pool fire, combustion in an open situation will normally proceed without explosion. Mixtures of gases or vapours with air within the explosive limits which are subsequently ignited will burn at normal flame velocity (a few m/s) to produce a ‘soft’ explosion, with minor material damage, often limited to scorching by the moving flame front. Injuries to personnel may well be more severe.

If the mixture (or a dust cloud) is confined, even if only by surface irregularities or local partial obstructions, significant pressure effects can occur. Fuel-air mixtures near to stoicheiometric composition and closely confined will develop pressures of several bar within milliseconds, and material damage will be severe. Unconfined vapour explosions of large dimensions may involve higher flame velocities and significant pressure effects, as shown in the Flixborough disaster.

See DUST EXPLOSION INCIDENTS
  PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION
  VAPOUR CLOUD EXPLOSIONS

Detonation is an extreme form of explosion where the propagation velocity becomes supersonic in gaseous, liquid or solid states. The temperatures and particularly pressures associated with detonation are higher by orders of magnitude than in deflagration. Energy release occurs in a few microseconds and the resulting shattering effects are characteristic of detonation. Deflagration may accelerate to detonation if the burning material and geometry of confinement are appropriate (endothermic compounds, long narrow vessels or pipelines).

See Acetylene (reference 9)
ENDOTHERMIC COMPOUNDS
EXPLOSIONS
UNIT PROCESS INCIDENTS

Factors of importance in preventing such thermal runaway reactions are mainly related to the control of reaction velocity and temperature within suitable limits. These may involve such considerations as adequate heating and particularly cooling capacity in both liquid and vapour phases of a reaction system; proportions of reactants and rates of addition (allowing for an induction period); use of solvents as diluents and to reduce viscosity of the reaction medium; adequate agitation and mixing in the reactor; control of reaction or distillation pressure; use of an inert atmosphere.

See AGITATION INCIDENTS

In some cases it is important not to overcool a reaction system, so that the energy of activation is maintained.

See Acetylene: Halogens (reference 1)

Adiabatic Systems

Because process heating is expensive, lagging is invariably applied to heated process vessels to minimise heat loss, particularly during long-term hot storage. Such adiabatic or near-adiabatic systems are potentially hazardous if materials of limited thermal stability, or which possess self-heating capability, are used in them. Insufficiently stabilised bulk-stored monomers come into the latter category.

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent
  POLYMERISATION INCIDENTS
  SELF-HEATING AND IGNITION INCIDENTS
  THERMAL STABILITY OF REACTION MIXTURES
  VIOLENT POLYMERISATION

Reactivity vs. Composition and Structure

The ability to predict reactivity and stability of chemical compounds from their composition and structure is as yet limited, so the ability accurately to foresee potential hazards during preparation, handling and processing of chemicals and their mixtures is also restricted. Although some considerable progress has been made in the use of computer programs to predict hazards, the best available approach for many practical purposes appears to be an initial appraisal based on analogy with, or extrapolation from, data for existing compounds and processes. This preliminary assessment can be supplemented with calorimetric instrumental examination, then bench-scale testing procedures for thermal stability applied to realistic reaction mixtures and processing conditions, should any doubt of safety persist. A wide range of equipment and techniques is now available for this purpose.

See ACCELERATING RATE CALORIMETRY
ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
COMPUTATION OF REACTIVE CHEMICAL HAZARDS
DIFFERENTIAL SCANNING CALORIMETRY
DIFFERENTIAL THERMAL ANALYSIS
MAXIMUM REACTION HEAT
REACTION SAFETY CALORIMETRY

It has long been recognised that instability in single compounds, or high reactivity in combinations of different materials, is usually associated with particular groupings of atoms or other features of molecular structure, such as high proportions or local concentrations of oxygen or nitrogen. Details of such features associated with explosive instability are collected under the heading EXPLOSIBILITY.

An approximate indication of likely instability in a compound may be gained from inspection of the empirical molecular formula to establish stoicheiometry.

See HIGH-NITROGEN COMPOUNDS
OXYGEN BALANCE

Endothermic compounds, formed as the energy-rich products of endothermic reactions, are thermodynamically unstable and may be liable to energetic decomposition with low energy of activation.

See ENDOTHERMIC COMPOUNDS

Reaction Mixtures

So far as reactivity between different compounds is concerned, some subdivision can be made on the basis of the chemical types involved. Oxidants (electron sinks) are undoubtedly the most common chemical type to be involved in hazardous incidents, the other components functioning as fuels or other electron sources. Air (21% oxygen) is the most widely dispersed oxidant, and air-reactivity may lead to either short- or long-term hazards.

Where reactivity of a compound is very high, oxidation may proceed so fast in air that ignition occurs.

See PYROPHORIC MATERIALS

Slow reaction with air may lead to the longer-term hazard of peroxide formation.

See AUTOXIDATION
PEROXIDATION INCIDENTS
PEROXIDES IN SOLVENTS
PEROXIDISABLE COMPOUNDS

Oxidants more concentrated than air are of greater hazard potential, and the extent of involvement of the common oxidants
Perchloric acid
Chlorine
Nitric acid
Hydrogen peroxide
Sulfuric acid
METAL CHLORATES

may be judged from the large number of incidents in the text involving each of them, as well as other OXIDANTS.

At the practical level, experimental oxidation reactions should be conducted to maintain in the reacting system a minimum oxygen balance consistent with other processing requirements. This may involve adding the oxidant slowly with appropriate mixing and cooling to the other reaction materials to maintain the minimum effective concentration of oxidant for the particular reaction. It will be essential to determine by a suitable diagnostic procedure that the desired reaction has become established, to prevent build-up of unused oxidant and a possible approach to the oxygen balance point.

See OXYGEN BALANCE

Reducants (rich electron sources) in conjunction with reducible materials (electron acceptors) feature rather less frequently than oxidants in hazardous incidents.

See REDUCANTS

Interaction of potent oxidants and reducants is invariably highly energetic and of high hazard potential.

See Dibenzoyl peroxide: Lithium tetrahydroaluminate
Hydrazine: Oxidants
REDOX REACTIONS
ROCKET PROPELLANTS

Similar considerations apply to those compounds which contain both oxidising and reducing functions in the same molecular structure.

See REDOX COMPOUNDS

Water is, after air, one of the most common reagents likely to come into contact with reactive materials, and several classes of compounds will react violently, particularly with restricted amounts of water.

See WATER-REACTIVE COMPOUNDS

Most of the above has been written with deliberate processing conditions in mind, but it must be remembered that the same considerations will apply, and perhaps to a greater degree, under the uncontrolled reaction conditions prevailing when accidental contact of reactive chemicals occurs in storage or transit.

Adequate planning is therefore necessary in storage arrangements to segregate oxidants from fuels and reducants, and fuels and combustible materials from compressed gases and water-reactive compounds. This will minimise the possibility of accidental contact and violent reaction arising from faulty containers or handling operations, and will prevent intractable problems in the event of fire in the storage areas.

See SAFE STORAGE OF CHEMICALS

Unexpected sources of ignition may lead to ignition of flammable materials during chemical processing or handling operations.

See FRICTIONAL IGNITION OF GASES
IGNITION SOURCES
SELF-HEATING AND IGNITION INCIDENTS
STATIC INITIATION INCIDENTS

Protective Measures

The need to provide protective measures will be directly related to the level of potential hazards which may be assessed from the procedures outlined above. Measures concerned with reaction control are frequently mentioned in the following text, but details of techniques and equipment for personal protection, though usually excluded from the scope of this work, are obviously of great importance.

Careful attention to such detail is necessary as a second line of defence against the effects of reactive hazards. The level of protection considered necessary may range from the essential and absolute minimum of effective eye protection, *via* the safety screen, fume cupboard or enclosed reactor, up to the ultimate of a remotely controlled and blast-resistant isolation cell (usually for high-pressure operations). In the absence of facilities appropriate to the assessed level of hazard, operations must be deferred until such facilities are available.

Volume 1

Specific Chemicals

(Elements and Compounds arranged in formula order)

EXPLANATORY NOTES

This volume gives detailed information on the hazardous properties of individual chemicals, either alone or in combination with other compounds. The items are arranged in order of the empirical formula (at right of second bold title line) which corresponds to the chemical name, or a synonym within parentheses, used as the first line bold title of each main entry; (nomenclature is now rather promiscuous since the systematisers have contrived to give many materials two or even three new names since the first edition was published, while the name used where chemicals are handled, as opposed to in lecture rooms, will be something else again). The 3 part number within square brackets at the left of the second title line is the CAS registry number, now being widely used to provide a reliable basis for establishing equivalence between differing chemical names and trade names for the same chemical compound (but note that one compound, within the terms of this work, may have numerous CAS numbers by virtue of isotopic composition, undefined stereo- and regio-chemistry or variant solvation levels). Lack of content within the square brackets indicates that a registry number has not yet been located, (or may not exist if CAS considers the compound insufficiently characterised, which is highly probable for materials which exploded during analysis) and (ion) after the number indicates that the main ion only has been located, rather than the specific title salt. Where possible, an alpahanumeric representation of the structure of the title compound is given at the centre of the third title line, otherwise a drawn structure.

A † prefixed to the chemical name indicates the existence of tabulated information on fire-related properties in Appendix 2. The † prefix is also appended to the entry (and any synonym) in the index in Appendix 4 of the chemicals appearing as title lines. Immediately under the title lines some references to sources of general safety-related data concerning use and handling precautions for the title chemical are given. The references to the series of *MCA Safety Data Sheets* are given in parentheses because the whole series was withdrawn in 1980, apparently on grounds other than obsolescence of the technical content. Since these data sheets are no longer available, alternative references are given where possible to the Data Sheets available from the National Safety Council *(NSC)*, Chicago; the Fire Protection Association *(FPA)*, London; to the appropriate page of 'Handling Chemicals Safely 1980' *(HCS 1980),* published in Holland; or to the new *Laboratory Hazard Data Sheet* series being published by the Royal Society of Chemistry *(RSC),* now in Cambridge. No new datasheets have been included since 1990, since distinction between the proliferation of sources would be invidious, most appear to have ben compiled my (mis)information (ne)scientists at their computers, connected to the world wide web, but not to a practised chemist who is familiar with the material in question. Fortunately, the manufacturer's data sheets, now supplied even by laboratory supply houses, are steadily improving and mean that reference to other similar sources is less needful

The first reference(s) and data given under the title lines refer to the hazards of the title material alone, or in the presence of air, unless stated otherwise. Where other (secondary) chemicals are involved with the title compound in a reactive incident, the name(s) follows in roman characters under the bold title entry. As in previous editions of this Handbook, where these secondary chemicals are described in group terms (e.g. Polynitroaryl compounds), reference to the alphabetical group entries now in Volume 2 may suggest other analogous possibilities of hazards. References to original or abstract literature then follow, and sufficient of the relevant information content is given to allow a general picture of the nature and degree of hazard to be seen.

Two features relevant to entries for pairs of reactive chemicals arise from the work of Prof. T. Yoshida in developing a method for the calculation of maximum reaction heats (MRH) possible for binary (or ternary) mixtures of chemicals, and the publication of his tabulated results. Where available for combinations existing in this text, these data are given opposite the name of the secondary chemical in the form MRH 2.9/22. This means that the calculated reaction heat is maximal at 2.9 kJ/g in a mixture containing 22% wt of the secondary reactant with 78% of the main (bold title) compound. The second feature is the inclusion of the secondary entry 'Other reactants' under which the extent of the information available in Yoshida's book for some 240 title compounds is given. More detail on the origin of these figures is given in Volume 2 under the entry MAXIMUM REACTION HEAT.

All temperatures in the text are expressed in degrees Celsius; pressures in bars, mbars or Pa; volumes in m^3, litres or ml; and energy as joules, kJ or MJ. Where appropriate, attention is drawn to closely similar or related materials or events by *See* or *See also* cross-references. Finally, if a title compound is a member of one of the general classes or groups in Volume 2, it is related to those by a *See other* cross-reference. If the compound is not strictly classifiable, a *See related* cross-reference establishes a less direct link to the group compound index lists in Volume 2, such compounds being prefixed in the lists by an asterisk. In relatively few cases, literature references (or further references) for individual compounds are in the alphabetical entries in Volume 2, and a *See entry* cross-reference leads to that entry with the literature reference. An alphabetical index of the chemical names used as bold titles in Volume 1, together with synonyms, is given in Appendix 4.

Details of corrections of typographical or factual errors, or of further items for inclusion in the text, will be welcomed, and a page which can be photocopied for this purpose will be found at the back of the book.

0001. Silver
[7440-22-4] **Ag**

Ag

Acetylenic compounds MRH Acetylene 8.70/99+
See ACETYLENIC COMPOUNDS

Aziridine
See Aziridine: Silver

Bromine azide
See Bromine azide

3-Bromopropyne
See 3-Bromopropyne: Metals

Carboxylic acids
Koffolt, J. H., private comm., 1965
Silver is incompatible with oxalic or tartaric acids, since the silver salts decompose on heating. Silver oxalate explodes at 140°C, and silver tartrate loses carbon dioxide.
See other METAL OXALATES

Chlorine trifluoride MRH 1.42/36
See Chlorine trifluoride: Metals

Copper, Ethylene glycol
See Ethylene glycol: Silvered copper wire

Electrolytes, Zinc
Britz, W. K. *et al., Chem. Abs.*, 1975, **83**, 150293
Causes of spontaneous combustion and other hazards of silver—zinc batteries were investigated.

Ethanol, Nitric acid
Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 334
Action of silver on nitric acid in presence of ethanol may form the readily detonable silver fulminate.
See Nitric acid: Alcohols
See also SILVER-CONTAINING EXPLOSIVES

Ethyl hydroperoxide
See Ethyl hydroperoxide: Silver

Ethylene oxide MRH 3.72/99+
See Ethylene oxide: Reference 4

Hydrogen peroxide MRH 1.59/99+
See Hydrogen peroxide: Metals

Iodoform
Grignard, 1935, Vol. 3, 320
In contact with finely divided (reduced) silver, incandescence occurs.

Other reactants

Yoshida, 1980, 103

MRH values for 7 combinations, largely with catalytically susceptible materials, are given.

Ozonides

See OZONIDES

Peroxomonosulfuric acid

See Peroxomonosulfuric acid: Catalysts

Peroxyformic acid MRH 5.69/100

See Peroxyformic acid: Metals

See other METALS

0002. Silver—aluminium alloy

[11144-29-9] **Ag—Al**

Ag—Al

1. Popov, E. I. *et al., Chem. Abs.*, 1977, **87**, 205143
2. Popov, E. I. *et al., Chem. Abs.*, 1980, **94**, 35622

Combustion and explosion hazards of the powdered alloy used in batteries were studied. Increase in silver content leads to higher values of the ignition temperature and COI [1,2].

See other ALLOYS, SILVER COMPOUNDS

0003. Silvered copper

[37218-25-0] **Ag—Cu**

Ag—Cu

Ethylene glycol

See Ethylene glycol: Silvered copper wire

See related ALLOYS

0004. Silver—thorium alloy

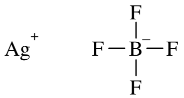
[12785-36-3] (1:2) **Ag—Th**

Ag—Th

See entry PYROPHORIC ALLOYS

0005. Silver tetrafluoroborate

[14104-20-2] **$AgBF_4$**



$Ag^+ \quad BF_4^-$

Preparative hazard

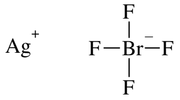
1. Meerwein, H. *et al., Arch. Pharm.*, 1958, **291**, 541—544
2. Lemal, D. M. *et al., Tetrahedron Lett.*, 1961, 776—777
3. Olah, G. A. *et al., J. Inorg. Nucl. Chem.*, 1960, **14**, 295—296

Experimental directions must be followed exactly to prevent violent spontaneous explosions during preparation of the salt from silver oxide and boron trifluoride etherate in nitromethane, according to the earlier method [1]. The later method [3] is generally safer than that in [2].

See other SILVER COMPOUNDS

0006. Silver tetrafluorobromate

[35967-89-6] **$AgBrF_4$**



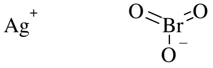
$Ag^+ \quad F-Br^-(F)_2-F$

See entry METAL POLYHALOHALOGENATES

See other SILVER COMPOUNDS

0007. Silver bromate

[7783-89-3] **$AgBrO_3$**



Other reactants

Yoshida, 1980, 133

MRH values for 16 combinations with oxidisable materials are given.

Sulfur compounds MRH Sulfur 2.0/12

1. Taradoire, F., *Bull. Soc. Chim. Fr.*, 1945, **12**, 94—95
2. Pascal, 1960, Vol. 13.1, 1004

The bromate is a powerful oxidant, and unstable mixtures with sulfur ignite at 73—75°C, and with disulfur dibromide on contact [1]. Hydrogen sulfide ignites on contact with the bromate [2].

See other METAL OXOHALOGENATES, SILVER COMPOUNDS

0008. Silver chloride

[7783-90-6] **AgCl**

$Ag^+ \qquad Cl^-$

Aluminium

See Aluminium: Silver chloride

Ammonia

1. Mellor, 1941, Vol. 3, 382
2. Kauffmann, G. B., *J. Chem. Educ.*, 1977, **54**, 132
3. Ranganathan, S. *et al., J. Chem. Educ.*, 1976, **53**, 347

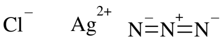
Exposure of ammoniacal silver chloride solutions to air or heat produces a black crystalline deposit of 'fulminating silver', mainly silver nitride, with silver diimide and silver amide also possibly present [1]. Attention is drawn [2] to the possible explosion hazard in a method of recovering silver from the chloride by passing an ammoniacal solution of the chloride through an ion exchange column to separate the $Ag(NH_3)^+$ ion, prior to elution as the nitrate [3]. It is essential to avoid letting the ammoniacal solution stand for several hours, either alone or on the column [2].

See Silver nitride

See other METAL HALIDES, SILVER COMPOUNDS

0009. Silver azide chloride

[67880-13-1] **$AgClN_3$**



Frierson, W. J. *et al., J. Amer. Chem. Soc.*, 1943, **65**, 1698

It is shock sensitive when dry.

See other METAL AZIDE HALIDES, SILVER COMPOUNDS

0010. Silver chlorite

[7783-91-7] **$AgClO_2$**

Alone, or Iodoalkanes

Levi, G. R., *Gazz. Chim. Ital. [2]*, 1923, **53**, 40

The salt is impact-sensitive, cannot be finely ground, and explodes at 105°C. Attempts to react silver chlorite with iodo-methane or -ethane caused explosions, immediate in the absence of solvents, or delayed in their presence.

Hydrochloric acid, or Sulfur

Mellor, 1941, Vol. 2, 284

It explodes in contact with hydrochloric acid or on rubbing with sulfur.

Non-metals

Pascal, 1960, Vol. 16, 264

Finely divided carbon, sulfur or red phosphorus are oxidised violently by silver chlorite.

See other CHLORITE SALTS, SILVER COMPOUNDS

0011. Silver chlorate

[7783-92-8] **$AgClO_3$**

Sorbe, 1968, 126

An explosive compound and powerful oxidant.

Ethylene glycol MRH 2.68/17

See Ethylene glycol: Oxidants

Other reactants

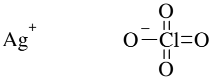
Yoshida, 1980, 69

MRH values for 17 combinations, largely with oxidisable materials, are given.

See other METAL CHLORATES, SILVER COMPOUNDS

0012. Silver perchlorate

[7783-93-9] **$AgClO_4$**



Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 2

It melts without decomposition although the enthalpy of conversion to silver chloride and oxygen appears to be about —0.5 kJ/g. An explosion while grinding the salt (which had not been in contact with organic materials) has been reported [1]. A powerful oxidant.

Acetic acid MRH 2.80/22

Mellor, 1956, Vol. 2, Suppl. 1, 616

The salt solvated with acetic acid is impact sensitive.

See Aromatic compounds, below

Alkynes, Mercury

Comyns, A. E. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 4324

Concentrated solutions of the perchlorate in 2-pentyne or 3-hexyne (complexes are formed) explode on contact with mercury.

See METAL ACETYLIDES

Aromatic compounds MRH Aniline 3.47/11, toluene 3.51/9

1. Sidgwick, 1950, 1234
2. Brinkley, S. R., *J. Amer. Chem. Soc.*, 1940, **62**, 3524
3. Peone, J. *et al., Inorg. Synth.*, 1974, **15**, 69
4. Stull, 1977, 22

Silver perchlorate forms solid complexes with aniline, pyridine, toluene, benzene and many other aromatic hydrocarbons [1]. A sample of the benzene complex exploded violently on crushing in a mortar. The ethanol complex also exploded similarly, and unspecified perchlorates dissolved in organic solvents were observed to explode [2].

Solutions of the perchlorate in benzene are said to be dangerously explosive [3], but this may be in error for the solid benzene complex. The energy released on decomposition of the benzene complex has been calculated as 3.4 kJ/g, some 75% of that for TNT [4].

Carbon tetrachloride, Hydrochloric acid
491M, 1975, 368
Silver perchlorate and carbon tetrachloride in presence of a little hydrochloric acid produce trichloromethyl perchlorate, which explodes at 40°C.
See Trichloromethyl perchlorate

1,2-Diaminoethane
491M, 1975, 368
Dropwise addition of the amine to the salt led to an explosion (possibly initiated by heat liberated by complex formation).

Diethyl ether
Heim, F., *Angew. Chem.*, 1957, **69**, 274
After crystallisation from ether, the material exploded violently on crushing in a mortar. It had been considered stable previously, since it melts without decomposition [1].

Dimethyl sulfoxide
Ahrland, S. *et al., Acta. Chem. Scand. A*, 1974, **28**, 825
The crystalline complex solvated with 2DMSO explodes with extreme violence if rubbed or scratched.
See Dimethyl sulfoxide: Metal oxosalts

Ethanol MRH 3.30/13
See Aromatic compounds, above

Other reactants
Yoshida, 1980, 81
MRH values for 20 combinations with oxidisable materials are given.

1,4-Oxathiane
Barnes, J. C. *et al., J. Chem. Soc. Pak.*, 1982, **4**, 103—113
The perchlorate forms complexes with 2, 3 or 4 mols of oxathiane which explode on heating.

Tetrachlorosilane, or Tetrabromosilane, or Titanium tetrachloride, and Diethyl ether
Schmeisser, M., *Angew. Chem.*, 1955, **67**, 499
Reaction gives explosive volatile organic perchlorates, probably ethyl perchlorate.
See ALKYL PERCHLORATES

Tetrasulfur tetraimide
See Tetrasulfurtetraimide—silver(I) perchlorate
See other METAL PERCHLORATES, OXIDANTS, SOLVATED OXOSALT INCIDENTS

0013. Silver fluoride

[7775-41-9] **AgF**

$Ag^+ \quad F^-$

Calcium hydride

See Calcium hydride: Silver halides

Non-metals

Mellor, 1941, Vol. 3, 389

Boron reacts explosively when ground with silver fluoride; silicon reacts violently.

Titanium

Mellor, 1941, Vol. 7, 20

Interaction at 320°C is incandescent.

See other METAL HALIDES, SILVER COMPOUNDS

0014. Silver difluoride

[7783-95-1] **AgF_2**

$F^- \; Ag^{2+} \; F^-$

Boron, Water

Tulis, A. J. *et al., Proc. 7th Symp. Explos. Pyrotechnics*, 1971, **3**(4), 1—12

Mixtures of boron and silver difluoride function as detonators when contacted with water.

Dimethyl sulfoxide

See Iodine pentafluoride: Dimethyl sulfoxide

Hydrocarbons, or Water

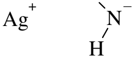
Priest, H. F. *Inorg. Synth.*, 1950, **3**, 176

It reacts even more vigorously with most substances than does cobalt fluoride.

See other METAL HALIDES, SILVER COMPOUNDS

0015. Silver amide

[65235-79-2] **AgH_2N**



$Ag^+ \quad H_2N^-$

Brauer, 1965, Vol. 2, 1045

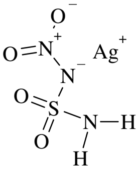
Extraordinarily explosive when dry.

See Nitrogen triiodide—silver amide

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0016. Silver *N*-nitrosulfuric diamidate

[ ] **$AgH_2N_3O_4S$**



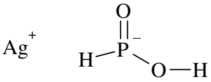
Sorbe, 1968, 120

The silver salt of the nitroamide is explosive.

See other *N*-METAL DERIVATIVES, *N*—NITRO COMPOUNDS, SILVER COMPOUNDS

0017. Silver phosphinate

[ ] **AgH_2O_2P**



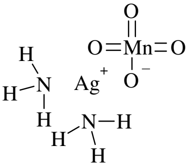
Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 335

Explosive, but less sensitive than the azide or fulminate.

See other METAL PHOSPHINATES, SILVER COMPOUNDS

0018. Diamminesilver permanganate

[ ] **$AgH_6MnN_2O_4$**



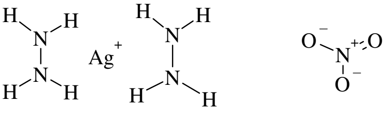
Pascal, 1960, Vol. 16, 1062

It may explode on impact or shock.

See other AMMINEMETAL OXOSALTS, SILVER COMPOUNDS

0019. Dihydrazinesilver nitrate

[31247-72-0] **$AgH_8N_5O_3$**



Gall, H. *et al., Z. Anorg. Chem.*, 1932, **206**, 376

The salt explodes at —1.5°C.

See other AMMINEMETAL OXOSALTS, SILVER COMPOUNDS

0020. Silver iodate

[7783-97-3] **$AgIO_3$**

Metals MRH Potassium 1.50/25, sodium 1.92/35

See Potassium: Oxidants
Sodium: Iodates

Other reactants

Yoshida, 1980, 194

MRH values for 16 combinations with oxidisable materials are given.

Tellurium

Pascal, 1960, Vol. 13.2, 1961

Interaction is violent.

See other METAL HALOGENATES, SILVER COMPOUNDS

0021. Silver permanganate

[7783-98-4] **$AgMnO_4$**

Sulfuric acid

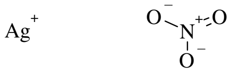
491M, 1975, 369

The moist salt exploded during drying over the concentrated acid in a vacuum desiccator, (presumably owing to formation of traces of manganese heptoxide from reaction with sulfuric acid vapour).

See other OXIDANTS, SILVER COMPOUNDS

0022. Silver nitrate

[7761-88-8] **$AgNO_3$**



HCS 1980, 822

Acetaldehyde

Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 336

Aqueous silver nitrate reacts with acetaldehyde to give explosive silver fulminate.

Acetylene and derivatives

Mellor, 1946, Vol. 5, 854

Silver nitrate (or other soluble salt) reacts with acetylene in presence of ammonia to form silver acetylide, a sensitive and powerful detonator when dry. In the absence of

ammonia, or when calcium acetylide is added to silver nitrate solution, explosive double salts of silver acetylide and silver nitrate are produced. Mercury(I) acetylide precipitates silver acetylide from the aqueous nitrate.
See 1,3-Butadiyne, and Buten-3-yne, both below
See METAL ACETYLIDES

Acrylonitrile
See Acrylonitrile: Silver nitrate

Aluminium
Laing, M., *J. Chem. Educ.*, 1994, **71**, 270
It is warned that a mixture of aluminium powder and silver nitrate is potentially as dangerous as that with magnesium, both being capable of producing > 8 kJ/g.
See Magnesium, Water; below

Ammonia MRH 1.46/29

1. *MCA Case History No. 2116*
2. *CISHC Chem. Safety Summ.*, 1976, **47**, 31
3. MacWilliam, E. A. *et al., Photogr. Sci. Eng.*, 1977, **21**, 221—224

A bottle containing Gomari tissue staining solution (ammoniacal silver nitrate) prepared 2 weeks previously exploded when disturbed. The solution must be prepared freshly each day, and discarded immediately after use with appropriate precautions [1]. A large quantity of ammoniacal silver nitrate solution exploded violently when disturbed by removing a glass rod [2]. However, it has now been shown that neither the solid precipitated during addition of ammonia to the nitrate, nor the redissolved complex, is sensitive to initiation by very severe shocks. This was so for fresh or aged solutions. The solids produced by total evaporation at 95°C or higher would explode only at above 100 kg cm shock force. A pH value above 12.9 is essential for separation of explosive precipitates, and this cannot be attained by addition of ammonia alone [3].
Silver(I) oxide: Ammonia, etc.
See SILVER-CONTAINING EXPLOSIVES (reference 2)

Ammonia, Ethanol
MCA Case History No. 1733
A silvering solution exploded when disturbed. This is a particularly dangerous mixture, because both silver nitride and silver fulminate could be formed.
See Ethanol, below

Ammonia, Sodium carbonate
Vasbinder, H., *Pharm. Weekblad*, 1952, **87**, 861—865
A mixture of the components in gum arabic solution (marking ink) exploded when warmed.

Ammonia, Sodium hydroxide

1. Milligan, T. W. *et al., J. Org. Chem.*, 1962, **27**, 4663
2. *MCA Case History No. 1554*
3. Morse, J. R., *School Sci. Rev.*, 1955, **37**(131), 147
4. Baldwin, J., *School Sci. Rev.*, 1967, **48**(165), 586

5. MacWilliam, E. A. *et al., Photogr. Sci. Eng.*, 1977, **21**, 221—224
6. Anon., *Univ. Safety Assoc. Safety News*, 1977, (8), 15—16

During preparation of an oxidising agent on a larger scale than described [1], addition of warm sodium hydroxide solution to warm ammoniacal silver nitrate with stirring caused immediate precipitation of black silver nitride which exploded [2]. Similar incidents had been reported previously [3], including one where explosion appeared to be initiated by addition of Devarda's alloy (Al—Cu—Zn) [4]. The explosive species separates at pH values above 12.9, only produced when alkali is added to ammoniacal silver solutions, or when silver oxide is dissolved with ammonia [5]. The Sommer & Market reagent mixture used to identify cellulose derivatives led to a severe explosion [6].

See Silver nitride

See also Ammonia: Silver compounds

See also SILVERING SOLUTIONS, TOLLENS' REAGENT

Arsenic

Mellor, 1941, Vol. 3, 470

A finely divided mixture with excess nitrate ignited when shaken out onto paper.

1,3-Butadiyne

See 1,3-Butadiyne: Silver nitrate

Buten-3-yne

See Buten-3-yne: Silver nitrate

Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Chlorosulfuric acid

Mellor, 1941, Vol. 3, 470

Interaction is violent, nitrosulfuric acid being formed.

Disilver ketenide

See Disilver ketenide—silver nitrate

Ethanol MRH 2.55/12

1. Tully, J. P., *Ind. Eng. Chem. (News Ed.)*, 1941, **19**, 250
2. Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 334
3. Garin, D. L. *et al., J. Chem. Educ.*, 1970, **47**, 741
4. Perrin, D. D. *et al., Chem. Brit.*, 1986, **22**, 1084; *Chem. Eng. News*, 1987, **65**(2), 2

Reclaimed silver nitrate crystals, damp with the alcohol used for washing, exploded violently when touched with a spatula, generating a strong smell of ethyl nitrate [1]. The explosion was attributed to formation of silver fulminate (which is produced on addition of ethanol to silver nitrate solutions). Ethyl nitrate may also have been involved. Alternatives to avoid ethanol washing of recovered silver nitrate are discussed [2], including use of 2-propanol [3]. Another case of explosion during filtration of silver nitrate purified by progressive dilution with ethanol of its aqueous solution has been reported. Initiation was by agitation of the slurry on a glass frit with a spatula [4].

See Silver fulminate

Magnesium, Water MRH 6.94/30

1. Marsden, F., private comm., 1973
2. Lyness, D. J. *et al., School Sci. Rev.*, 1953, **35**(125), 139

An intimate mixture of dry powdered magnesium and silver nitrate may ignite explosively on contact with a drop of water [1,2].

See other REDOX REACTIONS

Non-metals MRH Carbon 2.46/10, phosphorus (y) 3.89/18, sulfur 1.67/16

Mellor, 1941, Vol. 3, 469—473

Under a hammer blow, a mixture with charcoal ignites, while mixtures with phosphorus or sulfur explode, the latter violently.

Other reactants

Yoshida, 1980, 194

MRH values for 19 combinations with oxidisable materials are given.

Phosphine

Mellor, 1941, Vol. 3, 471

Rapid passage of gas into a conc. nitrate solution caused an explosion, or ignition of a slower gas stream. The explosion may have been caused by rapid oxidation of the precipitated silver phosphide derivative by the co-produced nitric acid or dinitrogen tetraoxide.

Phosphonium iodide

See Phosphonium iodide: Oxidants

Polymers

491M, 1975, 366

To assess suitability of plastic storage containers for distribution of silver nitrate, behaviour under fire exposure conditions of various polymers in contact with the salt was examined. All polymers tested burned vigorously.

Silver acetylide

See Silver acetylide—silver nitrate

Sodium dithionite

U.S. Chemical Safety and Investigation Board, *Report No 2003-08-I-RI*, 2004

An explosion and fire was initiated by tapping a vent line. It was concluded that silver nitrate almost certainly was the initiating oxidant, reacting with other materials which would have passed as dust into the vent. These included ammonium citrate, sodium dithionite, various organics, and ammonia. Although reaction with ammonia, producing fulminating silver or silver azide could not be precluded, sodium dithionite showed the easiest initiation of any unstable mixture tested, showing self heating from about room temperature. This mixture and the thermally more stable one with ammonium citrate both proved shock-sensitive.

Thiophene

Southern, T., private communication, 1990

A black solid is produced from these two reagents under influence of ultrasound (but not otherwise) which explodes violently on warming. It is apparently not silver acetylide.

Titanium

Shanley, E. S., *Chem. Eng. News*, 1990, **68**(16), 2

A titanium-containing sludge from a nitric acid bath was separated, before completely dry it exploded, killing a workman. Investigation showed the dry sludge to be a powerful explosive sensitive to heat, friction and impact, composed of about 60:40 silver nitrate:titanium.

See Titanium: Nitric acid

See other METAL NITRATES, SILVER COMPOUNDS

0023. Silver azide

[13863-88-2] **AgN_3**

$$\mathrm{Ag^{+}} \qquad \mathrm{\overset{-}{N}{=}\overset{+}{N}{=}N^{-}}$$

1. Mellor, 1940, Vol. 8, 349; 1967, Vol. 8, Suppl. 2, 47
2. Gray, P. *et al., Chem. & Ind.*, 1955, 1255
3. Kabanov, A. A. *et al., Russ. Chem. Rev.*, 1975, **44**, 538
4. Ryabykh, S. M. *et al., Chem. Abs.*, 1984, **100**, 194549

As a heavy metal azide, it is considerably endothermic (ΔH_f° + 279.5 kJ/mol, 1.86 kJ/g). While pure silver azide explodes at 340°C [1], the presence of impurities may cause explosion at 270°C. It is also impact-sensitive and explosions are usually violent [2]. Its use as a detonator has been proposed. Application of an electric field to crystals of the azide will detonate them, at down to —100°C [3], and it may be initiated by irradiation with electron pulses of nanosecond duration [4].

See other CATALYTIC IMPURITY INCIDENTS, IRRADIATION DECOMPOSITION INCIDENTS

Ammonia

Mellor, 1940, Vol. 8, 349

Solutions in aqueous ammonia become explosive around 100°C.

Chlorine azide

See Chlorine azide: Ammonia, etc.

Halogens

Mellor, 1940, Vol. 8, 336

Silver azide, itself a sensitive compound, is converted by ethereal iodine into the less stable and explosive compound, iodine azide. Similarly, contact with nitrogen-diluted bromine vapour gives bromine azide, often causing explosions.

See Silver azide chloride

Metal oxides, or Metal sulfides

Kurochin, E. S. *et al., Chem. Abs.*, 1974, **83**, 201390

Pure silver azide explodes at 340°C, but presence of below 10% of copper(I) or (II) oxides or sulfides, copper(I) selenide or bismuth(III) sulfide reduces the detonation temperature to 235°C. Concentrations of 10% of copper(II) oxide, copper(I) selenide or sulfide further reduced it to 200, 190 and 170°C, respectively.

Photosensitising dyes

Aleksandrov, E. *et al., Chem. Abs.*, 1974, **81**, 31755

In a study of dye-sensitised silver azide, it was found that many dyes caused explosions in the initial stages.

Sulfur dioxide

Mellor, 1940, Vol. 8, 349

Mixtures of the slightly soluble azide with liquid sulfur dioxide became explosive at elevated temperatures.

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES, SILVER COMPOUNDS

0024. Silver trisulfurpentanitridate

[ ] **AgN_5S_3**

Structure unknown

See 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine: Ammonia

See other N—S COMPOUNDS, SILVER COMPOUNDS

0025. Silver(II) oxide

[1301-96-8] **AgO**

$Ag^{2+} \quad O^{2-}$

Hydrogen sulfide

See Hydrogen sulfide: Metal oxides

See other METAL OXIDES, SILVER COMPOUNDS

0026. Silver sulfide

[21548-73-2] **AgS**

AgS

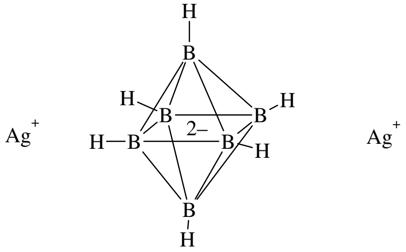
Potassium chlorate

See Potassium chlorate: Metal sulfides

See other METAL SULFIDES, SILVER COMPOUNDS

0027. Silver hexahydrohexaborate(2—)

[ ] **$Ag_2B_6H_6$**



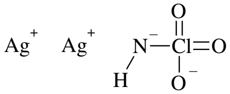
Bailar, 1973, Vol. 1, 808

It is a detonable salt.

See other COMPLEX HYDRIDES, SILVER COMPOUNDS

0028. Silver perchlorylamide

[25870-02-4] **Ag_2ClNO_3**

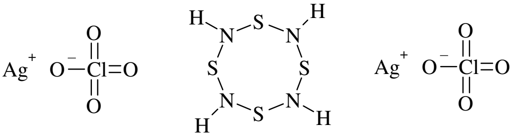


See entry PERCHLORYLAMIDE SALTS

See other SILVER COMPOUNDS

0029. Tetrasulfurtetraimide—silver perchlorate

[64867-41-0] **$Ag_2Cl_2H_4N_4O_8S_4$**



Nabi, S. N., *J. Chem. Soc., Dalton Trans.*, 1977, 1156

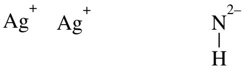
The complex detonates violently at 120°C.

See other SILVER COMPOUNDS

See related METAL PERCHLORATES, N—S COMPOUNDS

0030. Silver imide (μ-Imidodisilver)

[421553-79-9] **Ag_2HN**



$Ag^+ \quad Ag^+ \quad H{-}N^{2-}$

Bailar, 1973, Vol. 3, 101

It explodes very violently when dry.

See Silver(I) oxide: Ammonia (reference 2)

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0031. Silver hyponitrite

[7784-04-5] **$Ag_2N_2O_2$**

$Ag^+ \quad {}^-O{-}N{=}N{-}O^- \quad Ag^+$

See Hyponitrous acid

See other METAL OXONON-METALLATES, SILVER COMPOUNDS

0032. Silver(I) oxide

[20667-12-3] **Ag_2O**

$$Ag^{+} \quad O^{2-} \quad Ag^{+}$$

Aluminium

See Copper(II) oxide: Metals

Ammonia

1. Vasbinder, H., *Pharm. Weekblad*, 1952, **87**, 861—865
2. MacWilliam, E. A., *Photogr. Sci. Eng.*, 1977, **21**, 221—224

The clear solution, obtained by centrifuging a solution of the oxide in aqueous ammonia which had been treated with silver nitrate until precipitation started, exploded on two occasions after 10—14 days' storage in closed bottles in the dark. This was ascribed to slow precipitation of amorphous silver imide, which is very explosive even when wet [1]. When silver oxide is dissolved in ammonia solution, an extremely explosive precipitate (probably Ag_3N_4) will separate. The explosive behaviour is completely inhibited by presence of colloids or ammonium salts (acetate, carbonate, citrate or oxalate). Substitution of methylamine for ammonia does not give explosive materials [2].

See Silver nitrate: Ammonia, etc.

See also Ammonia: Silver compounds

Ammonia or Hydrazine, Ethanol

Silver oxide and ammonia or hydrazine slowly form explosive silver nitride and, in presence of alcohol, silver fulminate may also be produced.

See entry SILVER-CONTAINING EXPLOSIVES, SILVERING SOLUTIONS

Boron trifluoride etherate, Nitromethane

See Silver tetrafluoroborate

Carbon monoxide

Mellor, 1941, Vol. 3, 377

Carbon monoxide is exothermically oxidised over silver oxide, and the temperature may attain 300°C.

Chlorine, Ethylene

See Ethylene: Chlorine

Dichloromethylsilane

See Dichloromethylsilane: Oxidants

Hydrogen sulfide

See Hydrogen sulfide: Metal oxides

Magnesium

Mellor, 1941, Vol. 3, 378

Oxidation of magnesium proceeds explosively when warmed with silver oxide in a sealed tube.

Metal sulfides

Mellor, 1941, Vol. 3, 376

Mixtures with gold(III) sulfide, antimony sulfide or mercury(II) sulfide ignite on grinding.

Nitroalkanes

See NITROALKANES: Metal oxides

Non-metals

Mellor, 1941, Vol. 3, 376—377

Selenium, sulfur or phosphorus ignite on grinding with the oxide.

Potassium—sodium alloy

See Potassium—sodium alloy: Metal oxides

Seleninyl chloride

See Seleninyl chloride: Metal oxides

Selenium disulfide

Mellor, 1941, Vol. 3, 377

A mixture may ignite under impact.

See other METAL OXIDES, SILVER COMPOUNDS

0033. Silver peroxide

[25455-73-6] **Ag_2O_2**

$\mathrm{Ag^+}\quad \mathrm{\overset{-}{O}{-}\overset{-}{O}}\quad \mathrm{Ag^+}$

Poly(isobutene)

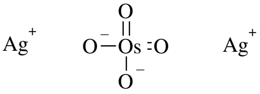
Mellinger, T., *Arbeitsschutz*, 1972, 248

Mixtures of silver peroxide with 1% of polyisobutene exploded on 3 separate occasions. Use of a halogenated polymer was safe.

See other METAL PEROXIDES

0034. Silver osmate

[ ] **Ag_2O_4Os**



$\mathrm{Ag^+}\quad \mathrm{^{-}O{-}Os(=O)_2{-}O^{-}}\quad \mathrm{Ag^+}$

Sorbe, 1968, 126

Explodes on impact or heating.

See other HEAVY METAL DERIVATIVES, SILVER COMPOUNDS

0035. Silver sulfide

[21548-73-2] **Ag_2S**

$Ag^+ \quad S^{2-} \quad Ag^+$

Potassium chlorate

See Potassium chlorate: Metal sulfides

See other METAL SULFIDES, SILVER COMPOUNDS

0036. Disilver pentatin undecaoxide

[ ] **$Ag_2Sn_5O_{11}$**

Structure unknown

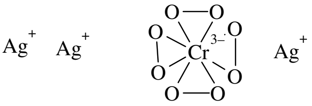
Mellor, 1941, Vol. 7, 418

The compound 'silver beta-stannate' is formed by long contact between solutions of silver and stannous nitrates, and loses water on heating, then decomposing explosively.

See other METAL OXIDES, SILVER COMPOUNDS

0037. Silver peroxochromate

[ ] **Ag_3CrO_8**



Sulfuric acid

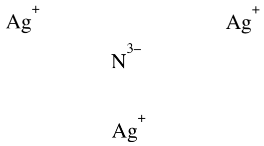
Riesenfeld, E. H. *et al., Ber.*, 1914, **47**, 548

In attempts to prepare 'perchromic acid', a mixture of silver (or barium) peroxochromate and 50% sulfuric acid prepared at —80°C reacted explosively on warming to about —30°C.

See other PEROXOACID SALTS, SILVER COMPOUNDS

0038. Silver nitride

[20737-02-4] **Ag_3N**



$Ag^+ \quad Ag^+ \quad N^{3-} \quad Ag^+$

Hahn, H. *et al., Z. Anorg. Chem.*, 1949, **258**, 77

Very sensitive to contact with hard objects, exploding when moist. An extremely sensitive explosive when dry, initiable by friction, impact or heating. The impure product produced by allowing ammoniacal silver oxide solution to stand seems even more sensitive, often exploding spontaneously in suspension.

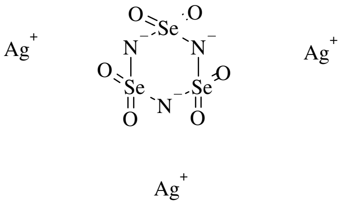
See Silver chloride: Ammonia

See also SILVER-CONTAINING EXPLOSIVES, SILVERING SOLUTIONS, TOLLENS' REAGENT

See other CATALYTIC IMPURITY INCIDENTS, *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0039. Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide ('Silver triselenimidate')

[ ] **$Ag_3N_3O_6Se_3$**



See Selenium difluoride dioxide: Ammonia

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0040. Trisilver tetranitride

[ ] **Ag_3N_4**

Ag^+

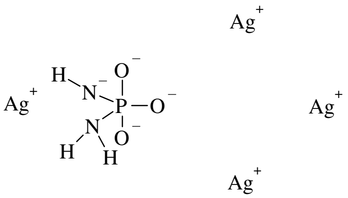
[39]

See Silver(I) oxide: Ammonia (reference 2)

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0041. Tetrasilver orthodiamidophosphate

[ ] **$Ag_4H_3N_2O_3P$**



Sulfuric acid

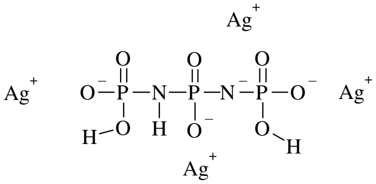
Mellor, 1940, Vol. 8, 705

Ignites with sulfuric acid.

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0042. Tetrasilver diimidotriphosphate

[ ] **$Ag_4H_3N_2O_8P_3$**



Alone, or Sulfuric acid

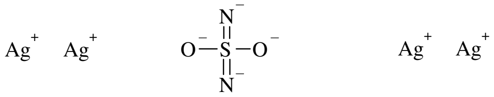
Mellor, 1940, Vol. 8, 705; 1971, Vol. 8, Suppl. 3, 787

The dry material explodes on heating, and ignites in contact with sulfuric acid. The molecule contains one N—Ag bond.

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0043. Tetrasilver diimidodioxosulfate

[ ] **$Ag_4N_2O_2S$**



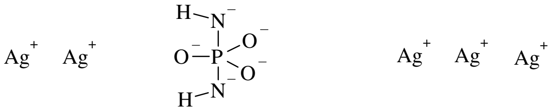
Nachbauer, E. *et al., Angew. Chem. (Intern. Ed.)*, 1973, **12**, 339

The dry salt explodes on friction or impact.

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0044. Pentasilver orthodiamidophosphate

[ ] **$Ag_5H_2N_2O_3P$**



Alone, or Sulfuric acid

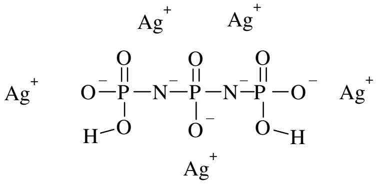
Stokes, H. N., *Amer. Chem. J.*, 1895, **17**, 275

Explodes on heating, friction or contact with sulfuric acid.

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0045. Pentasilver diimidotriphosphate

[ ] **$Ag_5H_2N_2O_8P_3$**



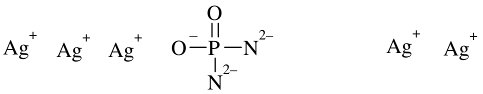
Alone, or Sulfuric acid

Mellor, 1940, Vol. 8, 705; 1971, Vol. 8, Suppl. 3, 787

The salt is explosive and may readily be initiated by friction, heat or contact with sulfuric acid. The molecule contains two N—Ag bonds.

0046. Pentasilver diamidophosphate

[ ] **$Ag_5N_2O_2P$**



1. Bailar, 1973, Vol. 8, 455
2. Mellor, 1940, Vol. 8, 705

The salt contains 85% silver and four N—Ag bonds [1], and detonates readily on friction, heating or contact with sulfuric acid [2].

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0047. Heptasilver nitrate octaoxide

[12258-22-9] **Ag_7NO_{11}**

$(Ag_3O_4)_2.AgNO_3$

Alone, or Sulfides, or Non-metals

Mellor, 1941, Vol. 3, 483—485

The crystalline product produced by electrolytic oxidation of silver nitrate (and possibly as formulated) detonates feebly at 110°C. Mixtures with phosphorus and sulfur explode on impact, hydrogen sulfide ignites on contact and antimony trisulfide ignites when ground with the salt.

See other SILVER COMPOUNDS

See related METAL NITRATES

0048. Aluminium

[7429-90-5] **Al**

Al

HCS 1980, 135 (powder)

1. *Haz. Chem. Data*, 1975, 44
2. *Dust Explosion Prevention: Aluminum Powder*, NFPA Standard Codes 65, 651, both 1987
3. Popov, E. I. *et al., Chem. Abs.*, 1975, **82**, 61411
4. Ida, K. *et al., Japan Kokai*, 1975, 75 13 233
5. Steffens, H. D. *et al., Chem. Abs.*, 1979, **90**, 209354
6. Scherbakov, V. K. *et al., Chem. Abs.*, 1979, **91**, 76322
7. Barton, J. A. *et al., Chem. Brit.*, 1986, **22**, 647—650
8. May, D. C. *et al., J. Haz. Mat.*, 1987, **17**(1), 61—88
9. *See entry* DUST EXPLOSION INCIDENTS (reference 22)
10. Dahn, C. J. *et al., P/M Sci. Technol Briefs*, 2000, **2**(5), 10
11. Ingignoli, W. *et al., Chem. Abs.*, 2001, **135**s, 375841v

Finely divided aluminium powder or dust forms highly explosive dispersions in air [1], and all aspects of prevention of aluminium dust explosions are covered in 2 US National Fire Codes [2]. The effects on ignition properties of impurities introduced by recycled metal used to prepare dust were studied [3]. Pyrophoricity is eliminated by surface coating aluminium powder with polystyrene [4]. Explosion hazards involved in arc and flame spraying of the powder are analysed and discussed [5], and the effect of surface oxide layers on flammability was studied [6]. The causes of a severe explosion in 1983 in a plant producing fine aluminium powder are analysed, and improvements in safety practices discussed [7]. A number of fires and explosions involving aluminium dust arising from grinding, polishing and buffing operations are discussed, and precautions detailed [8]. Atomised and flake aluminium powders attain maximum explosion pressures of 5.7 and 8.6 bar, respectively, both with maximum rates of pressure rise exceeding 1.36 kbar/s [9]. An article considers predicting dust explosion hazards in consideration of particle shape, coating additives or mixtures [10]. Although accidents may suggest that unconfined aluminium dust/air mixtures can detonate, it has as yet proved impossible to demonstrate this experimentally at laboratory scale [11].

Air, Hydrocarbons

Lamnevik, S., *Chem. Abs.*, 1982, **96**, 202034

Presence of dispersed aluminium powder in propane—air or butane—air mixtures enhances the detonative properties of stoichiometric mixtures.

Air, Water

1. Turetzky, M., private comm., 1987
2. *MARS Database*, 1998, short report 028

Fine aluminium dust and chippings from precision surface machining operations were air-transported to a cyclone collection system with outlet bag filters for the dust, and the cyclone contents were discharged into metal scrap bins. Sparks from a portable grinding machine ignited aluminium dust on a maintenance platform, and use of a carbon dioxide extinguisher on the fire transferred it into a metal scrap bin below. Heat from this larger fire activated the automatic water sprinkler system, and contact of the water (89% oxygen) with the burning metal liberated hydrogen, which, after mixing with air, exploded. This primary explosion created an aluminium dust cloud which exploded forcefully, creating larger dust clouds and eventually involving the contents of the other scrap bins and 2 of the dust filter bags, leading to at least 4 separate tertiary explosions in all. Structural damage to adjacent buildings and vehicles was extensive. The dry collection system was replaced by a wet one [1].

A different scenario involving these three occurred when lightning struck an aluminium foundry. It is supposed that this dispersed molten metal droplets in air, which then exploded with the estimated force of 200 kg TNT, causing damage which allowed remaining molten metal to fall into the wet casting pit, producing a second explosion of half the power of the first [2].

Alkali, Phosphorus compounds
See Drain cleaner, cola, below

Alkalis
Aluminium dissolves readily, and exothermically, in aqueous alkali, generating highly combustible hydrogen and hydrides of other non-metals and metalloids which may be present. This has given rise to several incidents below.
See also STATUARY

Aluminium halides, Carbon oxides
Guntz, A. *et al., Compt. rend.*, 1897, **124**, 187—190
Aluminium powder burns when heated in carbon dioxide, and presence of aluminium chloride or aluminium iodide vapour in carbon monoxide or carbon dioxide accelerates the reaction to incandescence.

Ammonium nitrate MRH 8.70/75
Mellor, 1946, Vol. 5, 219
Mixtures with the powdered metal are used as an explosive, sometimes with the addition of carbon or hydrocarbons, or other oxidants.
See Ammonium nitrate: Metals

Ammonium nitrate, Calcium nitrate, Formamide
See Calcium nitrate: Aluminium, etc.

Ammonium peroxodisulfate
See Ammonium peroxodisulfate: Aluminium

Antimony or Arsenic
Matignon, C., *Compt. rend.*, 1900, **130**, 1393
Powdered aluminium reacts violently on heating with antimony or arsenic.

Antimony trichloride
Matignon, C., *Compt. rend.*, 1900, **130**, 1393
The metal powder ignites in antimony trichloride vapour.

Arsenic trioxide, Sodium arsenate, Sodium hydroxide
MCA Case History No. 1832

An aluminium ladder was used (instead of the usual wooden one) to gain access to a tank containing the alkaline arsenical mixture. Hydrogen produced by alkaline attack on the ladder generated arsine, which poisoned the three workers involved.

Barium peroxide

See Barium peroxide: Metals

Bismuth

Mellor, 1947, Vol. 9, 626

The finely divided mixture of metals produced by hydrogen reduction of co-precipitated bismuth and aluminium hydroxides is pyrophoric.

Butanol

1. Luberoff, B. J., private comm., 1964
2. Bogart, M. J. P., *Chem. Eng. Progr.*, 1988, (2), 82

Butanol, used as a solvent in an autoclave preparation at around 100°C, severely attacked the aluminium gasket, liberating hydrogen which caused a sharp rise in pressure. Other alcohols would behave similarly, forming the aluminium alkoxide [1]. On a larger scale, a distillation column, constructed in aluminium by chemical engineers who neglected chemistry, fell apart within 24 hours of start-up [2].

See other CORROSION INCIDENTS

Calcium oxide, Chromium oxide, Sodium chlorate MRH 10.7/67

Nolan, 1983, Case History 174

In a thermite process to produce chromium metal, the mechanically-mixed ingredients were ignited in a large crucible and the reaction proceeded smoothly. When the mixer broke down, manual mixing was used but gave poorer dispersion of the constituents. An explosion after ignition is attributed to a high local concentration of sodium chlorate and aluminium powder in the mixture.

See other THERMITE REACTIONS

Carbon dioxide

See Carbon dioxide: Metals

Carbon dioxide, Sodium peroxide

See Sodium peroxide: Metals, etc.

Carbon disulfide

Matignon, C., *Compt. rend.*, 1900, **130**, 1391

Aluminium powder ignites in carbon disulfide vapour.

Carbon tetrachloride, Methanol

See Methanol: Carbon tetrachloride, Metals

Carbon, Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Catalytic metals

1. *491M*, 1975, 28
2. Kirk-Othmer (3rd ed.), 1982, Vol. 19, 495

At the m.p. of aluminium (600°C) an aluminium-sheathed palladium thermocouple formed an alloy with a flash and an exotherm to 2800°C [1]. The use of thin layers of palladium or platinum on aluminium foil or wire as igniters derives from the intense heat of alloy formation, which is sufficient to melt the intermetallic compounds [2].

Chloroformamidinium nitrate
See Chloroformamidinium nitrate (reference 2)

Copper, Sulfur
Donohue, P. C., US Pat. 3 932 291, 1973
During preparation of aluminium copper(I) disulfide from the elements in an air-free silica tube at 900—1000°C, initial heating must be slow to prevent explosion of the tube by internal pressure of unreacted sulfur vapour.

Copper(I) oxide
Haws, L. D. *et al., Proc. 6th Int. Pyrotech. Semin.*, 1978, 209—222
Technical aspects of the use of aluminium—copper(I) oxide thermite devices are detailed.
See Copper(I) oxide: Aluminium

Copper(II) oxide MRH 3.29/82

1. Anon., *Chem. Age.*, 1932, **27**, 23
2. Scamaton, W. B. *et al., Chem. Abs.*, 1980, **92**, 8484
3. Peterson, W. S., *Light Met.* (Warrendale, PA), 1987, 699—701

A mixture of aluminium powder and hot copper oxide exploded violently during mixing with a steel shovel on an iron plate. The frictional mixing initiated the thermite-like mixture [1]. Such mixtures are now used in electro-explosive devices [2]. Two cases of violent explosions after adding scrap copper to molten aluminium are discussed. In both cases, when some undissolved copper with adhering aluminium and oxide dross was removed from the furnace, the explosions occurred outside the melting furnace [3].
See Metal oxides, etc., below

Diborane
See Diborane: Metals

Dichloromethane
Piotrowski, A. M. *et al., J. Org. Chem.*, 1988, **53**, 2829—2835
Conditions are described for the safe reaction of aluminium powder with dichloromethane to give bis(dichloroalumino)methane in high yield. Derivatives of this compound are effective methyleneating agents for ketones.
See Halocarbons, below

Diethyl ether
Murdock, T. O., Ph.D. Thesis, Univ. N. Dakota, 1977 (*Diss. Abs. B*, 1978, **39**, 1291)
The aluminium—solvent slurry produced by metal atom/solvent co-condensation at —196°C is so reactive that oxygen is abstracted from the solvent ether as the mixture is allowed to melt. Hydrocarbon solvents are more suitable (but halocarbon solvents would react explosively).

Disulfur dibromide

See Disulfur dibromide: Metals

Drain cleaner, Cola

1. Utterbuck, P., Internet, 1997
2. Editor's comments
3. Faller, H. *et al., Gefahrstoffe - Reinhalt. Luft*, 2000, **60**(7-8), 301

A student mixed aluminium foil and drain cleaner in a soft drink bottle, which started emitting gas. Another student carried the bottle outside and was claimed to have been overcome by the toxic fumes [1]. Most drain cleaners are alkalis, so that aluminium will dissolve to produce hydrogen. The bleach that it is is suggested may have been present will produce no toxic fumes in alkali, and one would be surprised to find arsenic or antimony compounds present. If the collapse was not purely hysterical, the remaining, though remote, possibility would be phosphine. The soft drink the bottle had contained was one of the many perhaps best described as impure dilute phosphoric acid [2]. Subsequent unconnected study of cleaning agents showed that a combination of alkali and phosphate applied to aluminium can, indeed, generate significant levels of phosphine [3].

Explosives

1. Stettbacher, A., *Chem. Abs.*, 1944, **38**, 4445_4
2. Muraour, H., *Chem. Abs.*, 1944, **38**, 4445_7

The addition of substantial amounts (up to 32%) of aluminium powder to conventional explosives enhances the energy release by up to 100% [1], involving high temperature reduction of liberated carbon dioxide and water by the metal [2].

Formic acid

Matignon, C., *Compt. rend.*, 1900, **130**, 1392

The metal reduces the acid (itself a reducant) with incandescence

Halocarbons

1. Anon., *Angew. Chem.*, 1950, **62**, 584
2. Anon., *Chem. Age*, 1950, **63**, 155
3. Anon., *Chem. Eng. News*, 1954, **32**, 258
4. *Pot. Incid. Rep.*, ASESB, 1968, **39**
5. Anon., *Chem. Eng. News*, 1955, **33**, 942
6. Eiseman, B. J., *J. Amer. Soc. Htg. Refr. Air Condg. Eng.*, 1963, **5**, 63
7. Eiseman, B. J., *Chem. Eng. News*, 1961, **39**(27), 44
8. Laccabue, J. R., *Fluorolube—Aluminium Detonation Point: Report 7E.1500*, San Diego, Gen. Dynamics, 1958
9. Atwell, V. J., *Chem. Eng. News*, 1954, **32**, 1824
10. ICI Mond Div., private comm., 1973
11. Anon., *Ind. Acc. Prev. Bull. RoSPA*, 1953, **21**, 60
12. Wendon, G. W., private comm., 1973
13. Coffee, R. D., *Loss Prev.*, 1971, **5**, 113
14. Schwab, R. F., ibid., 113
15. Corley, R., ibid., 114

16. Heinrich, H. J., *Arbeitsschutz*, 1966, 156—157
17. Lamoroux, A. *et al., Mém. Poudres*, 1957, **39**, 435—445
18. Hamstead, A. C. *et al., Corrosion*, 1958, **14**, 189t—190t
19. Hartmann, I., *Ind. Eng. Chem.*, 1948, **40**, 756
20. *MCA Case History No. 2160*
21. Arias, A., *Ind. Eng. Chem., Prod. Res. Dev.*, 1976, **15**, 150
22. Wendon, G. W., *Ind. Eng. Chem., Prod. Res. Dev.*, 1977, **16**, 112
23. Arias, A., *Ind. Eng. Chem., Prod. Res. Dev.*, 1977, **16**, 112
24. Archer, W. L., Paper 47, 1—11, presented at *Corrosion/78*, Houston, March 6—10, 1978
25. Anon. *Univ. Safety Assoc. Newsletter*, 1982, (16), 5
26. Stull, 1977, 22
27. Cardillo, P., *et al., J. Loss Prevention*, 1992, **5**(2), 81

MRH Chloromethane 2.46/85, bromomethane 1.33/91, chloroform 3.84/82, carbon tetrachloride 4.15/91, carbon tetrafluoride 6.48/71, dichlorodifluoromethane 5.39/77, trichlorofluoromethane 4.76/79, trichloroethylene 4.10/83, trichlorofluoroethane 4.98/77, 1,2-dichloropropene 3.30/86, *o*-dichlorobenzene 2.67/89

Heating aluminium powder with carbon tetrachloride, chloromethane or carbon tetrachloride—chloroform mixtures in closed systems to 152°C may cause an explosion, particularly if traces of aluminium chloride are present [1]. A mixture of carbon tetrachloride and aluminium powder exploded during ball-milling [2], and it was later shown that heavy impact would detonate the mixture [3]. Mixtures with fluorotrichloroethane and with trichlorotrifluoroethane will flash or spark on heavy impact [4]. A virtually unvented aluminium tank containing a 4:1:2 mixture of *o*-dichlorobenzene, 1,2-dichloroethane and 1,2-dichloropropane exploded violently 7 days after filling. This was attributed to formation of aluminium chloride which catalysed further accelerating attack on the aluminium tank [5]. An analysis of the likely course of the Friedel-Crafts reaction and calculation of the likely heat release (29.1 kJ/mol) has been published [26].

In a dichlorodifluoromethane system, frictional wear exposed fresh metal surfaces on an aluminium compressor impellor, causing an exothermic reaction which melted much of the impellor. Later tests showed similar results, decreasing in order of intensity, with: tetrafluoromethane; chlorodifluoromethane; bromotrifluoromethane; dichlorodifluoromethane; 1,2-difluorotetrafluoroethane; 1,1,2-trichlorotrifluoroethane [6]. In similar tests, molten aluminium dropped into liquid dichlorodifluoromethane burned incandescently below the liquid [7]. Aluminium bearing surfaces under load react explosively with polytrifluoroethylene greases or oils. The inactive oxide film will be removed from the metal by friction, and hot spots will initiate reaction [8]. An attempt to scale up the methylation of 2-methylpropane with chloromethane in presence of aluminium chloride and aluminium went out of control and detonated, destroying the autoclave. The preparation had been done on a smaller scale on 20 previous occasions without incident [9].

Violent decomposition, with evolution of hydrogen chloride, may occur when 1,1,1-trichloroethane comes into contact with aluminium or its alloys with magnesium [10]. Aluminium-dusty overalls were cleaned by immersion in trichloroethylene. During subsequent drying, violent ignition occurred. This was attributed to presence of free hydrogen chloride in the solvent, which reacted to produce aluminium chloride [10]. This is known to catalyse polymerisation of trichloroethylene, producing more hydrogen chloride and heat. The reaction is self-accelerating and can develop a temperature of 1350°C [11]. Trichloroethylene cleaning baths must be kept neutral with sodium carbonate, and free of aluminium dust. Halocarbon solvents now available with added stabilisers (probably amines) show a reduced tendency to react with aluminium powder [12].

Aluminium powder undergoes an exothermic and uncontrollable reaction with dichloromethane above 95°C under appropriate pressure [13]. Several cases of violent reaction between aluminium and trichloroethylene or tetrachloroethylene in vapour degreasers have been noted [14]. Chloromethane in liquefied storage diffused 70 m along a nitrogen inerting line into the pressure regulator. Interaction with aluminium components of the regulator formed alkylaluminium compounds which ignited when the regulator was dismantled [15]. An explosion in an aluminium degreasing plant using tetrachloroethylene was attributed to overheating of residues on the heating coils. Subsequent tests showed that simultaneous presence of water and aluminium chloride in an aluminium powder—tetrachloroethylene mixture lowered the initiation temperature to below 250°C. Presence of cutting oils reduced it below 150°C, and a temperature of 300°C was reached within 100 min [16].

Reaction of aluminium powder with hexachloroethane in alcohol is not initially violent, but may become so [17]. An aluminium transfer pipe failed after a few hours' service carrying refined 1,2-dichloropropane in warm weather. The corrosive attack was simulated and studied under laboratory conditions [18]. In dichlorodifluoromethane vapour, aluminium dust ignited at 580°C, and suspensions of the dust in the vapour gave strong explosions when sparked [19]. A fire occurred at a liquid outlet from a 40 m^3 mild steel tanker of chloromethane. This was traced to the presence of trimethylaluminium produced by interaction of chloromethane and (unsuspected) aluminium baffle plates in the tanker [20]. A proposal to prepare pure aluminium chloride by ball-milling aluminium in carbon tetrachloride [21] was criticised [22] as potentially hazardous. Possible modifications (use of inert solvents, continuously fed mills, etc.) to improve the procedure were suggested [23]. The reaction mechanism of attack and inhibition in aluminium—1,1,1-trichloroethane systems has been investigated [24]. An attempt to clean a motor assembly containing an aluminium alloy gearwheel by soaking overnight in 1,1,1-trichloroethane led to gross degradation of the assembly [25].

A tabulation of theoretically hazardous halocarbon/aluminium combinations, and estimates of safe dilutions, calculated by the CHETAH program is reported [27].

See Bromomethane: Metals
See Dichloromethane, above
See COMPUTATION OF REACTIVE CHEMICAL HAZARDS
See other CORROSION INCIDENTS, METAL—HALOCARBON INCIDENTS

Halogens MRH Bromine 1.96/90, chlorine 5.23/80

1. Mellor, 1946, Vol. 2, 92, 135; Vol. 5, 209
2. Azmathulla, S. *et al., J. Chem. Educ.*, 1955, **32**, 447; *School Sci. Rev.*, 1956, **38**(134), 107
3. Hammerton, C. M., ibid, 1957, **38**(136), 459

Aluminium powder ignites in chlorine without heating, and foil reacts vigorously with liquid bromine at 15°C, and incandesces on warming in the vapour [1]. The metal and iodine react violently in the presence of water, either as liquid, vapour or that present in hydrated salts [2]. Moistening a powdered mixture causes incandescence and will initiate a thermite mixture [3].
See Iodine: Aluminium, Diethyl ether

Hydrochloric acid or Hydrofluoric acid
Kirk-Othmer, 1963, Vol. 1, 952
The metal is attacked violently by the aqueous acids.

Hydrogen chloride MRH 3.05/80
Batty, G.F., private comm., 1972
Erroneous use of aluminium instead of alumina pellets in a hydrogen chloride purification reactor caused a vigorous exothermic reaction which distorted the steel reactor shell.

Interhalogens
See Bromine pentafluoride: Acids, etc.
Chlorine fluoride: Aluminium
Iodine chloride: Metals
Iodine heptafluoride: Metals
Iodine pentafluoride: Metals

Iron, Water
Chen, W. Y. *et al., Ind. Eng. Chem.*, 1955, **47**(7), 32A
A sludge of aluminium dust (containing iron and sand) removed from castings in water was found, during summer weather, to undergo sudden exotherms to 95°C with hydrogen evolution. Similar effects with aluminium-sprayed steel plates exposed to water were attributed to electrolytic action, as addition of iron filings to a slurry of aluminium in water caused self heating and hydrogen evolution to occur.
See Water, below
See other CORROSION INCIDENTS

Iron(III) chloride
See Iron(III) chloride: aluminium

Mercury(II) salts
Woelfel, W. C., *J. Chem. Educ.*, 1967, **44**, 484
Aluminium foil is unsuitable as a packing material in contact with mercury(II) salts in presence of moisture, when vigorous amalgamation ensues.
See Aluminium amalgam (reference 2)
See other CORROSION INCIDENTS

Metal nitrates, Potassium perchlorate, Water
Johansson, S. R. *et al., Chem. Abs.*, 1973, **78**, 18435
A pyrotechnic mixture of aluminium powder with potassium perchlorate, barium nitrate, potassium nitrate and water exploded after 24 h storage under water. Tests revealed the exothermic interaction of finely divided aluminium with nitrate and

water to produce ammonia and aluminium hydroxide. Under the conditions prevailing in the stored mixture, the reaction would be expected to accelerate, finally involving the perchlorate as oxidant and causing ignition of the mixture.

Metal nitrates, Sulfur, Water

Anon., *Chem. Eng. News*, 1954, **32**, 258

Aluminium powder, barium nitrate, potassium nitrate, sulfur and vegetable adhesives, mixed to a paste with water, exploded on 2 occasions. Laboratory investigation showed initial interaction of water and aluminium to produce hydrogen. It was supposed that nascent hydrogen reduced the nitrates present, increasing the alkalinity and thence the rate of attack on aluminium, the reaction becoming self-accelerating. Cause of ignition was unknown. Other examples of interaction of aluminium with water are known.

See Iron, Water, above; Water, below

See other CORROSION INCIDENTS

Metal oxides or Oxosalts or Sulfides

1. Mellor, 1946, Vol. 5, 217
2. Price, D. J. *et al., Chem. Met. Eng.*, 1923, **29**, 878

MRH Chromium trioxide 6.15/79, iron(II) oxide 3.01/80, iron(II)(III) oxide 3.38/76, calcium sulfate 5.73/65, sodium carbonate 2.92/67, sodium nitrate 8.32/65, sodium sulfate 5.27/66

Many metal oxo-compounds (nitrates, oxides and particularly sulfates) and sulfides are reduced violently or explosively (i.e. undergo 'thermite' reaction) on heating an intimate mixture with aluminium powder to a suitably high temperature to initiate the reaction. Contact of massive aluminium with molten salts may give explosions [1]. Application of sodium carbonate to molten (red hot) aluminium caused an explosion [2].

See Iron(III) oxide: Aluminium

See Sodium sulfate, below

See other MOLTEN SALT BATHS, THERMITE REACTIONS

Methanol

Médard, L. *Mém. Poudres*, 1951, **33**, 490—503 (Engl. translation HSE 11270, 1986 available from HSE/LIS)

The explosive nature of mixtures of aluminum or magnesium with methanol or water is detailed.

See Magnesium: Methanol

Niobium oxide, Sulfur

491M, 1975, 28

A mixture caused a serious fire.

See Metal oxides, etc., above

Nitro compounds, Water

Hajek, V. *et al., Research*, 1951, **4**, 186—191

Dry mixtures of picric acid and aluminium powder are inert, but addition of water causes ignition after a delay dependent upon the quantity added. Other nitro compounds and nitrates are discussed in this context.

Non-metal halides MRH Phosphorus pentachloride 2.76/83

1. Matignon, C., *Compt. rend.*, 1900, **130**, 1393
2. Lenher, V. *et al., J. Amer. Chem. Soc.*, 1926, **48**, 1553
3. Berger, E., *Compt. rend.*, 1920, **170**, 29

Powdered aluminium ignites in the vapour of arsenic trichloride or sulfur dichloride, and incandesces in phosphorus trichloride vapour [1]. Above 80°C, aluminium reacts incandescently with diselenium dichloride [2]. The powder ignites in contact with phosphorus pentachloride [3].

Non-metals

Matignon, C., *Compt. rend.*, 1900, **130**, 1393—1394

Powdered aluminium reacts violently with phosphorus, sulfur or selenium, and a mixture of powdered metal with red phosphorus exploded when severely shocked.

Oleic acid

de Ment, J., *J. Chem. Educ.*, 1956, **36**, 308

Shortly after mixing the two, an explosion occurred, but this could not be repeated. The acid may have been peroxidised.

Other reactants

Yoshida, 1980, 29

MRH values calculated for 44 combinations, largely with oxidants, are given.

Oxidants MRH values show % of oxidant

1. Kirshenbaum, 1956, 4, 13
2. Mellor, 1947, Vol. 2, 310
3. Annikov, V. E. *et al., Chem. Abs.*, 1976, **85**, 145389
4. Nakamura, H. *et al., Chem. Abs.*, 1985, **102**, 97779

Mixtures of aluminium powder with liquid chlorine, dinitrogen tetraoxide or tetranitromethane are detonable explosives, but not as powerful as aluminium—liquid oxygen mixtures, some of which exceed TNT in effect by a factor of 3 to 4 [1]. Mixtures of the powdered metal and various bromates may explode on impact, heating or friction. Iodates and chlorates act similarly [2]. Detonation properties of gelled slurries of aluminium powder in aqueous nitrate or perchlorate salt solutions have been studied [3]. Reactions of aluminium powder with potassium chlorate or potassium perchlorate have been studied by thermal analysis [4].

For other combinations,

See Halogens, above; Oxygen, below

Ammonium peroxodisulfate: Aluminium, etc.	
Nitryl fluoride: Metals	
Potassium chlorate: Metals	MRH 9.20/70
Potassium perchlorate: Aluminium, or: Metal powders	MRH 9.96/67
Sodium chlorate: Aluminium, Rubber	MRH (no rubber) 10.71/67
Sodium nitrate: Aluminium	MRH 8.32/65
Sodium peroxide: Aluminium, etc., or: Metals	MRH 4.56/81
Zinc peroxide: Alone, or Metals	

See other REDOX REACTIONS

Oxygen

1. Phillips, B. R. *et al., Combust. Flame*, 1979, **35**(3), 249—258
2. Ames Lab Yellow Alert 990217b, Internet, 1999

Metal powders or fibres ignite in an oxygen-fed resonance tube [1]. There have been fires in aluminium pressure regulators for oxygen. Aluminium and its alloys can become flammable at as low a pressure as 2 bar. Aluminium regulators are being replaced by brass, use of aluminium cylinders is still regarded as safe [2].

Oxygen, Water

Aleshim, M. A. *et al., Chem. Abs.*, 1979, **91**, 76312

Injection of oxygen is used to initiate the metal—water reaction in rocket propulsion systems.

Paint

See Zinc: Paint primer base

Palladium

See Catalytic metals, above

Polytetrafluoroethylene

1. Pittaluga, F. *et al., Termotechnica*, 1981, **25**, 332—334
2. Schwartz, A., Internet, 1996

A mixture of aluminium powder and PTFE has been evaluated as an underwater missile propellant [1]. It is suggested that using PTFE tape to lubricate and seal aluminium screw threads is inadvisable [2].

See Halocarbons, above

2-Propanol

1. Wilds, A. L., *Org. React.*, 1944, **2**, 198
2. Muir, G. D., private comm., 1968
3. Anon., *Safety Digest Univ. Safety Assoc.* 1994, (50), 21

Dissolution of aluminium in 2-propanol to give the isopropoxide is rather exothermic, but often subject to an induction period similar to that in preparation of Grignard reagents [1]. Only small amounts of aluminium should be present until reaction begins [2]. A canister of Video Display Unit Cleaner exploded in a cupboard. This is thought to have been because of faulty interior lacquer which allowed the propanol containing cleaner to attack the aluminium can, generating heat and hydrogen [3].

See Butanol; Methanol; both above

See Magnesium: Methanol

Silicon steel

Partington, 1967, 418

Aluminium is added (0.1%) to molten steel to remove dissolved oxygen and nitrogen to prevent blowholes in castings. It reacts very violently with silicon steels.

Silver chloride MRH 0.67/94

Anon., *Chem. Eng. News*, 1954, **32**, 258

An intimate mixture of the two powders may lead to reaction of explosive violence, unless excess aluminium is present (but note low MRH value).

Sodium acetylide
See Sodium acetylide: Metals

Sodium dithionite, Water
See Sodium dithionite: Aluminium, Water

Sodium diuranate
Gray, L. W., *Rept. DP-1485*, Richmond (Va), NTIS, 1978
During outgassing of scrap uranium—aluminium cermet reactor cores, powerful exotherms led to melting of 9 cores. It was found that the incident was initiated by reactions at 350°C between aluminium powder and sodium diuranate, which released enough heat to initiate subsequent exothermic reduction of ammonium uranyl hexafluoride, sodium nitrate, uranium oxide and vanadium trioxide by aluminium, leading to core melting.

Sodium hydroxide
1. *MCA Case History No. 1115*
2. *MCA Case History No. 1888*

In an incident involving corrosive attack on aluminium by sodium hydroxide solution, the vigorous evolution of hydrogen was noticed before a tank trailer (supposed to be mild steel) had perforated [1]. Corrosion caused failure of an aluminium coupling between a pressure gauge and a pump, causing personal contamination [2].

Sodium sulfate MRH 5.27/66
Kohlmeyer, E. J., *Aluminium*, 1942, **24**, 361—362
The violent explosion experienced when an 8:3 molar mixture of metal powder and salt was heated to 800°C was attributed to thermal dissociation (at up to 3000°C) of the metal sulfide(s) formed as primary product(s).
See other THERMITE REACTIONS

Steel
1. *MCA Case Histories Nos. 2161, 2184* (same incident)
2. Bailey, J. C., *Met. Mater.*, 1978, (Oct.), 26—27

A joint between a mild steel valve screwed onto an aluminium pipe was leaking a resin—solvent mixture, and when the joint was tightened with a wrench, a flash fire occurred. This was attributed to generation of sparks by a thermite reaction between the rusted steel valve and the aluminium pipe when the joint was tightened [1]. Hazards involved in the use of aluminium-sprayed steel are reviewed [2].

Sulfur MRH 4.81/64
Read, C. W. W., *School Sci. Rev.*, 1940, **21**(83), 977
The violent interaction of aluminium powder with sulfur on heating is considered to be too dangerous for a school experiment.

Uranium compounds
See Sodium diuranate, above

Water

1. *MCA Case History No. 462*
2. Shidlovskii, A. A., *Chem. Abs.*, 1947, **41**, 1105d
3. Bamberger, M. *et al., Z. Angew. Chem.*, 1913, **26**, 353—355
4. Gibson, 1969, 2
5. Pittaluga, F. *et al., Termotechnica*, 1977, **31**, 306—312
6. Sukhov, A. V., *Chem. Abs.*, 1978, **88**, 193939
7. Tompa, A. S. *et al., J. Haz. Mat.*, 1978, **2**, 197—215
8. Meguro, T. *et al., Chem. Abs.*, 1980, **90**, 8505
9. Lemmon, A. W., *Light Met.* (New York), 1980, 817—836
10. Boxley, G. *et al., Light Met.* (New York), 859—868
11. Epstein, S. G. *et al., Light Met.* (Warrendale Pa), 1987, 693—698; *ibid.,* 1993, 845
12. Epstein, S. G., *Light Met.* (Warrendale, Pa), 1995, 885
13. Ikata, K., *Chem. Abs.*, 1993, **118**, 127778
14. Breault, R. *et al., Light Met.* (Warrendale, Pa), 1995, 903
15. Hughes, D. T. *et al., IMechE Conf. Trans.*, 1995, (2), 73
16. Taylor, F. R. *et al., Rept. ARAED-TR-87022*, 1—26, 1988;

Cans of aluminium paint contaminated with water contained a considerable pressure of hydrogen from interaction of finely divided metal and moisture [1]. Mixtures of powdered aluminium and water can be caused to explode powerfully by initiation with a boosted detonator [2]. A propellant explosive composed of aluminium and water has been patented [13]. During granulation of aluminium by pouring the molten metal through a sieve into water, a violent explosion occurred. This was attributed to steam trapped in the cooling metal [3], but see references [9,10]. Moist finely divided aluminium may ignite in air [4]. The aluminium—steam reaction was evaluated for power generation purposes, a peak steam temperature of over 1000°C being attained [5]. The combustion of aluminium in steam has been studied in detail [6]. In a study of reaction of metal powder with water at 100—110°C in presence of various salts, pH values above 9.5 increased the rate of hydrogen evolution [7]. Hazards of storing aluminium powders and pastes in contact with water under alkaline or acid conditions were studied [8]. Investigations of the explosion mechanism when molten aluminium contacts water have been described [9,10,11], and plant incidents since 1940 are presented [11,12]. A study of hazards of transport of molten aluminium in possibly wet 'torpedoes' is available [14]. Investigation of aluminium alloyed with lithium or calcium revealed a more energetic explosion of the melt with water, but did not conclusively demonstrate easier initiation [15]. The use of organic coatings on aluminium or magnesium powder in pyrotechnic compositions prevents reaction with atmospheric moisture and problems resulting from hydrogen evolution [16].

See other CORROSION INCIDENTS, MOLTEN METAL EXPLOSIONS

Zinc

MCA Case History No. 1722

Ball-milling aluminium—zinc (not stated if alloy or mixture) with inadequate inerting arrangements led to fires during operation or discharge of the mill.

See other METALS, REDUCANTS

0049. Aluminium—cobalt alloy (Raney cobalt alloy)

[37271-59-3] 50:50; [12043-56-0] Al_5Co; [73730-53-7] Al_2Co Al—Co

Al—Co

The finely powdered Raney cobalt alloy is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

0050. Aluminium—copper—zinc alloy (Devarda's alloy)

[8049-11-4] Al—Cu—Zn

Al—Cu—Zn

See DEVARDA'S ALLOY
Silver nitrate: Ammonia, etc.
See other ALLOYS

0051. Aluminium amalgam (Aluminium—mercury alloy)

[12003-69-9] (1:1) Al—Hg

Al—Hg

1. Neely, T. A. *et al., Org. Synth.*, 1965, **45**, 109
2. Calder, A. *et al., Org. Synth.*, 1975, **52**, 78

The amalgamated aluminium wool remaining from preparation of triphenylaluminium will rapidly oxidise and become hot on exposure to air. Careful disposal is necessary [1]. Amalgamated aluminium foil may be pyrophoric and should be kept moist and used immediately [2].
See other ALLOYS

0052. Aluminium—lithium alloy

[103760-93-6] (7:1 atom ratio, 3.7% Li) Al—Li

Al—Li

Water

Jacoby, J. E. *et al.*, Can. Pat. CA 1 225 8166, 1987 (*Chem. Abs.*, 1988, **108**, 42436)
The molten alloy (2—3% Li) explodes violently if cooled by contact with water, but not if cooled by ethylene glycol containing less than 25% of water.
See other ALLOYS

0053. Aluminium—magnesium alloy

[12042-38-5] (1:3) Al—Mg

Al—Mg

The finely powdered alloy is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

Barium nitrate
See Barium nitrate, Aluminium—magnesium alloy

Iron(III) oxide, Water
Maischak, K. D. *et al., Neue Huette*, 1970, **15**, 662—665
Accidental contact of the molten alloy (26% Al) with a wet rusty iron surface caused violent explosions with brilliant light emission. Initial evolution of steam, causing fine dispersion of the alloy, then interaction of the fine metals with rust in a 'thermite' reaction, were postulated as likely stages. Direct interaction of the magnesium (74%) with steam may also have been involved.
See other THERMITE REACTIONS

Water
Long, G. C., *Spectrum* (Pretoria), 1980, **18**, 30
In a school demonstration, an alloy pencil sharpener body (ignited in a flame) continues to burn vigorously in steam.
See other ALLOYS

0054. Aluminium—magnesium—zinc alloy

[ ] **Al—Mg—Zn**

Al—Mg—Zn

Rusted steel
Yoshino, H. *et al., Chem. Abs.*, 1966, **64**, 14017j
Impact of an alloy containing 6% Al and 3% Zn with rusted steel caused incendive sparks which ignited LPG—air mixtures in 11 out of 20 attempts.
See IGNITION SOURCES, THERMITE REACTIONS

0055. Aluminium—nickel alloys (Raney nickel alloys)

[12635-29-9] **Al—Ni**

Al—Ni

HCS 1980, 807

Water
Anon., *Angew. Chem. (Nachr.)*, 1968, **16**, 2
Heating moist Raney nickel alloy containing 20% aluminium in an autoclave under hydrogen caused the aluminium and water to interact explosively, generating 1 kbar pressure of hydrogen.
See also HYDROGENATION CATALYSTS
See other ALLOYS

0056. Aluminium—titanium alloys

[12003-96-2] (1:1) **Al—Ti**

Al—Ti

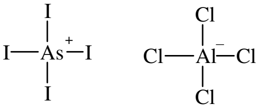
Su, Y-q. *et al., Chem. Abs.*, 2004, **140**, 97452u
The heat of alloying can be enough to cause explosive projection of melt from crucibles during alloy formation.

Oxidants

Mellor, 1941, Vol. 7, 20—21
Alloys ranging from Al_3Ti_2 to Al_4Ti have been described, which ignite or incandesce on heating in chlorine; or bromine or iodine vapour; (or hydrogen chloride); or oxygen.
See other ALLOYS

0057. Tetraiodoarsonium tetrachloroaluminate

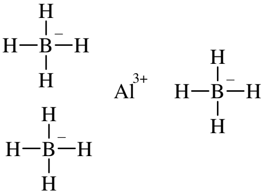
[124687-11-2] **$AlAsCl_4I_4$**



Klapötke, T. *et al., Angew. Chem. (Int.)*, 1989, **101**(12), 1742
Decomposes spontaneously at —78°C. Low temperature photolysis led to violent explosions on warming.
See other IODINE COMPOUNDS

0058. Aluminium tetrahydroborate

[16962-07-5] **AlB_3H_{12}**



1. Schlessinger, H. I. *et al., J. Amer. Chem. Soc.*, 1940, **62**, 3421
2. Badin, F. J. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 2950

The vapour is spontaneously flammable in air [1], and explodes in oxygen, but only in presence of traces of moisture [2].

Alkenes, Oxygen

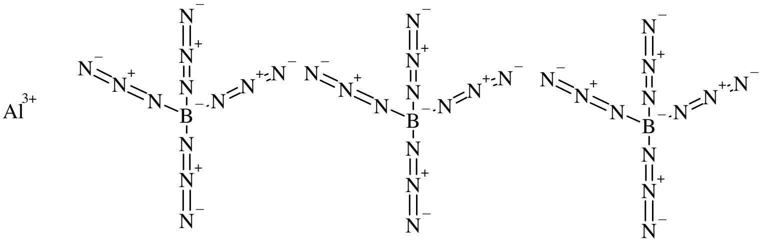
Gaylord, 1956, 26

The tetrahydroborate reacts with alkenes and, in presence of oxygen, combustion is initiated even in absence of moisture. Butene explodes after an induction period, while butadiene explodes immediately.
See other INDUCTION PERIOD INCIDENTS

Dimethylaminoborane
Burg, A. B. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 953
Reaction with dimethylaminoborane or dimethylaminodiborane gives an oily mixture which ignites in air and reacts violently with water.

Water
Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 4
Interaction at ambient temperature is explosive.
See other COMPLEX HYDRIDES

0059. Aluminium tetraazidoborate
[67849-01-8] **AlB_3N_{36}**



Mellor, 1967, Vol. 8, Suppl. 2, 2
A very shock sensitive explosive, containing nearly 90 wt% of nitrogen.
See other HIGH-NITROGEN COMPOUNDS, NON-METAL AZIDES

0060. Aluminium bromide
[7727-15-3] **$AlBr_3$**

Al^{3+} Br^- Br^- Br^-

Dichloromethane
Kramer, G. M. *et al., Acc. Chem. Res.*, 1986, **19**(3), 78—84
Solutions of aluminium bromide in dichloromethane used as a catalyst in hydride-transfer equilibrium experiments should be kept cold, as a potentially dangerous exothermic halide exchange reaction occurs on warming.

Water
Nicholson, D. G. *et al., Inorg. Synth.*, 1950, **3**, 35
The anhydrous bromide should be destroyed by melting and pouring slowly into running water. Hydrolysis is very violent and may destroy the container if water is added to it.
See other METAL HALIDES

0061. Aluminium dichloride hydride diethyl etherate

[13497-97-7] (solvent-free) **$AlCl_2H.C_4H_{10}O$**

Dibenzyl ether

Marconi, W. *et al., Ann. Chim.*, 1965, **55**, 897

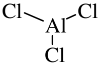
During attempted reductive cleavage of the ether with aluminium dichloride hydride etherate an explosion occurred. Peroxides may have been present in the susceptible ether.

See other PEROXIDATION INCIDENTS

See related COMPLEX HYDRIDES

0062. Aluminium chloride

[7446-70-0] **$AlCl_3$**



(*MCA SD-62*, 1956); *NSC 435*, 1978; *HCS 1980*, 130; *RSC Lab. Hazards Data Sheet No 72*, 1988

1. Popov, P. V., *Chem. Abs.*, 1947, **41**, 6723d
2. Kitching, A. F., *School Sci. Rev.*, 1930, **12**(45), 79
3. Bailar, 1973, Vol. 1, 1019

Long storage of the anhydrous salt in closed containers caused apparently spontaneous decomposition and occasional explosion on opening [1,2]. This seems likely to have arisen from slow diffusion of moisture (MW 18) in through the closure and pressurisation of the container by the liberated HCl which because of its higher MW (36.5) would diffuse out at a slower rate. The need is emphasised for care in experiments in which the chloride is heated in sealed tubes. High internal pressure may be generated, not only by its vapour pressure and pressure of desorbed hydrogen chloride, but also by the near doubling in volume which occurs when the chloride melts to the monomer [3].

Alkenes

Jenkins, P. A., private. comm., 1975

Mixtures of C_4 alkene isomers (largely isobutene) are polymerised commercially in contact with low levels of aluminium chloride (or other Lewis acid) catalysts. The highly exothermic runaway reactions occasionally experienced in practice are caused by events leading to the production of high local levels of catalyst. Rapid increases in temperature and pressure of 160°C and 18 bar, respectively, have been observed experimentally when alkenes are brought into contact with excess solid aluminium chloride. The runaway reaction appears to be more severe in the vapour phase, and a considerable amount of catalytic degradation contributes to the overall large exotherm.

See other POLYMERISATION INCIDENTS, RUNAWAY REACTIONS

Aluminium oxide, Carbon oxides
See Aluminium: Aluminium halides, Carbon oxides

Aluminium, Sodium peroxide
See Sodium peroxide: Aluminium, etc.

Benzene, Carbon tetrachloride
Nolan, 1983, Case history 105
Triphenylmethyl chloride was manufactured by a Friedel-Crafts reaction of benzene and carbon tetrachloride with excess aluminium chloride. Owing to an operating fault, all the carbon tetrachloride was added to the other reactants without agitation but with water cooling. When the agitator was started, two explosions followed. The first was from the sudden exotherm and gas evolution on mixing the reactants, and this damaged the heat exchangers and allowed ingress of cooling water, leading to a second explosion on contact with the aluminium chloride.
See also TRIPHENYLMETHYL CHLORIDES
See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS, GAS EVOLUTION INCIDENTS (reference 2) and Water below

Benzoyl chloride, Naphthalene
Clar, E. *et al., Tetrahedron*, 1974, **30**, 3296
During preparation of 1,5-dibenzoylnaphthalene, addition of aluminium chloride to a mixture of benzoyl chloride and naphthalene must be effected above the m.p. of the mixture to avoid a violent reaction.

Ethylene oxide
See Ethylene oxide: Contaminants

Ethylenimine, Substituted anilines
See Ethylenimine, Aluminium chloride, etc.

Nitrobenzene

1. Riethman, J. *et al., Chem. Ing. Tech.*, 1974, **48**, 729
2. Eigenmann, K. *et al., Proc. Int. Symp. Simulation*, 436, Zurich, Acta Press, 1975
3. Finck, P. *et al., Proc. Symp. Safety Chem. Ind.*, 17—25, Mulhouse, 1978
4. *See entry* SELF-ACCELERATING REACTIONS
5. Nolan, 1983, Case history 104

Mixtures of nitrobenzene and aluminium chloride are thermally unstable and may lead to explosive decomposition. Subsequent to an incident involving rupture of a 4000 l vessel, the decomposition reaction was investigated and a 3-stage mechanism involving formation and subsequent polymerisation of 2- and 4-chloronitrosobenzene was proposed [1]. Further chemical and thermodynamic work [2,3] on the thermal degradation of nitrobenzene—aluminium chloride addition compounds formed in Friedel-Crafts reactions shows that it is characterised by a slow multi-step decomposition reaction above 90°C, which self-accelerates with high exothermicity producing azo- and azoxy-polymers. Simulation of the original incident suggested that the pressure in the reactor probably increased from 3 to 40 bar in 5 s [4]. Nitrobenzene was added to a 2.2 kl reactor in readiness for a Friedel-Crafts reaction, but it leaked away through a faulty bottom valve. Aluminium chloride and a reactant, hexamethyltetralin were added, but when the agitator stopped (solid complex formation), the absence of the nitrobenzene solvent was realised. More nitrobenzene was being sucked in to the reactor when the exotherm from the reaction with aluminium chloride pressurised the reactor, boiled and ignited the limited amount of nitrobenzene, and shattered a glass fitting [5].

See other AGITATION INCIDENTS, POLYMERISATION INCIDENTS

Nitrobenzene, Phenol

Anon., *Chem. Eng. News*, 1953, **31**, 4915

Addition of aluminium chloride to a large volume of recovered nitrobenzene containing 5% of phenol caused a violent explosion. Experiment showed that mixtures containing all 3 components reacted violently at 120°C.

Nitromethane

See Aluminium chloride—Nitromethane

Other reactants

Yoshida, 1980, 52

MRH values calculated for 12 combinations with oxidants are given.

Oxygen difluoride

See Oxygen difluoride: Halogens, etc.

Perchlorylbenzene

See Perchlorylbenzene: Aluminium chloride

Phenyl azide

See Phenyl azide: Lewis acids

Sodium tetrahydroborate

See Sodium tetrahydroborate: Aluminium chloride, etc.

Water

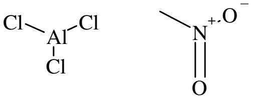
1. Anon., *Ind. Eng. Chem. (News Ed.)*, 1934, **12**, 194
2. Anon., *Loss Prev. Bull.*, 1980, (035), 9
3. Reza, A. *et al.*, *Proceedings of 36th Annual Loss Prevention Symposium*, 2002, 401, Amer. Inst. Chem. Eng.

An unopened bottle of anhydrous aluminium chloride erupted when the rubber bung with which it was sealed was removed. The accumulation of pressure was attributed to absorption of moisture by the anhydrous chloride before packing (but see comment following text of masthead reference 2). The presence of an adsorbed layer of moisture in the bottle used for packing may have contributed. Reaction with water is violently exothermic [1]. The unsuspected presence of 100 kg of the chloride in a vessel led to bursting of a glass vent when the vessel was being flushed with water [2]. An attempt to use steam to clear a sludge of aluminium chloride, aluminium and hydrocarbons at the bottom of a Friedel-Crafts alkylation reactor led to an explosion and fire. Investigation showed hydrolysis of aluminium chloride the principal cause [3].

See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS, METAL HALIDES

0063. Aluminium chloride—nitromethane

[3495-54-3] **$AlCl_3.CH_3NO_2$**



An alkene

Cowen, F. M. *et al., Chem. Eng. News*, 1948, **26**, 2257

A gaseous alkene was passed into a cooled autoclave containing the complex, initially with agitation, and later without. Later, when the alkene was admitted to a pressure of 5.6 bar at 2°C, a slight exotherm occurred, followed by an explosion. The autoclave contents were completely carbonised. Mixtures of ethylene, aluminium chloride and nitromethane had exploded previously, but at 75°C.

See Ethylene: Aluminium chloride, Catalysts

Carbon monoxide, Phenol

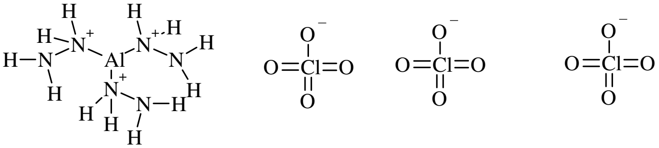
Webb, H. F., *Chem. Eng. News*, 1977, **55**(12), 4

An attempt to formylate phenol by heating a mixture with nitromethane and aluminium chloride in an autoclave under carbon monoxide at 100 bar pressure at 110°C led to a high-energy explosion after 30 min.

See related NITROALKANES

0064. Trihydrazinealuminium perchlorate

[85962-45-4] **$AlCl_3H_{12}N_6O_{12}$**



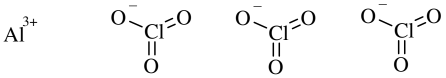
Ind. Inst. Sci., Indian Pat. IN 150422, 1982

Useful as a propellant oxidant.

See other AMMINEMETAL OXOSALTS, REDOX COMPOUNDS

0065. Aluminium chlorate

[15477-33-5] **$AlCl_3O_9$**



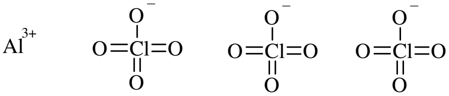
Sidgwick, 1950, 428

During evaporation, its aqueous solution evolves chlorine dioxide, and eventually explodes.

See other METAL CHLORATES

0066. Aluminium perchlorate

[14452-39-2] **$AlCl_3O_{12}$**



Dimethyl sulfoxide

See Dimethyl sulfoxide: Metal oxosalts

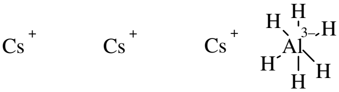
Hydrazine

See Trihydrazinealuminium perchlorate

See other METAL PERCHLORATES

0067. Caesium hexahydroaluminate(3—)

[53436-80-9] **$AlCs_3H_6$**

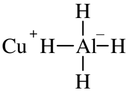


See Potassium hexahydroaluminate(3—)

See other COMPLEX HYDRIDES

0068. Copper(I) tetrahydroaluminate

[62126-20-9] **$AlCuH_4$**



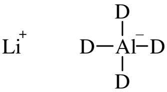
Aubry, J. *et al., Compt. rend.*, 1954, **238**, 2535

The unstable hydride decomposed at —70°C, and ignited on contact with air.

See other COMPLEX HYDRIDES

0069. Lithium tetradeuteroaluminate

[14128-54-2] **AlD_4Li**

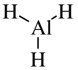


Leleu, Cahiers, 1977, (86), 99

It may ignite in moist air.

See related COMPLEX HYDRIDES

0070. Aluminium hydride
[7784-21-6] **AlH_3**



1. Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **54**(1), 54A
2. Gibson, 1968, 66

It is very unstable and has been known to decompose spontaneously at ambient temperature with explosive violence. Its complexes (particularly the diethyl etherate) are considerably more stable [1]. The hydride ignites in air with or without oxygen enrichment [2].

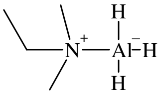
See Aluminium hydride—trimethylamine
Aluminium hydride—diethyl ether

Carbon dioxide, Methyl ethers
Barbaras, G. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 877
Presence of carbon dioxide in solutions of the hydride in dimethyl or bis(2-methoxyethyl) ether can cause a violent decomposition on warming the residue from evaporation. Presence of aluminium chloride tends to increase the vigour of decomposition to explosion. Lithium tetrahydroaluminate may behave similarly, but is generally more stable.
See Lithium tetrahydroaluminate (reference 8)

Carbon dioxide, or Sodium hydrogen carbonate
Thompson, B. T. *et al., Polyhedron*, 1983, **2**, 619—621
At elevated temperatures, the hydride reduces carbon dioxide or sodium hydrogencarbonate to methane and ethane. The latter are probably the explosive reaction products produced when carbon dioxide extinguishers are used on LAH fires.
See other GAS EVOLUTION INCIDENTS

Tetrazole derivatives
Fetter, N. R. *et al.*, US Pat. 3 396 170, 1968
The 1:1 complexes arising from interaction of the hydride (as a complex with ether or trimethylamine) and various tetrazole derivatives are explosive. Tetrazoles mentioned are 2-methyl-, 2-ethyl-, 5-ethyl-, 2-methyl-5-vinyl-, 5-amino-2-ethyl-, 1-alkyl-5-amino-, and 5-cyano-2-methyl-tetrazole.
See TETRAZOLES
See other METAL HYDRIDES

0071. Alane—*N,N*-dimethylethylamine ((*N,N*-Dimethylethanamine)trihydroaluminium)
[124330-23-0] **$AlH_3.C_4H_{11}N$**



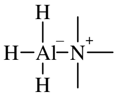
1. Frigo, D. M., *et al., Chem. Mater.*, 1994, **6**(2), 190
2. Senzaki, Y. *et al., Inorg. Synth.*, 1997, **31**, 74

Not generally pyrophoric, unless dropped on vermiculite, the complex decomposes slowly in the liquid phase to generate considerable pressures of hydrogen. It appears much more stable in the vapour phase [1]. It also ignites on contact with water [2]

See related METAL HYDRIDES

0072. Aluminium hydride—trimethylamine

[17013-07-9] **$AlH_3.C_3H_9N$**



Water

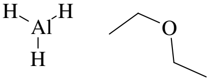
Ruff, J. K., *Inorg. Synth.*, 1967, **9**, 34

It ignites in moist air and is explosively hydrolysed by water.

See related METAL HYDRIDES

0073. Aluminium hydride—diethyl ether

[26351-01-9] **$AlH_3.C_4H_{10}O$**



Water

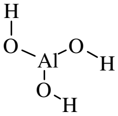
Schmidt, D. L. *et al., Inorg. Synth.*, 1973, **14**, 51

Interaction of the solid with water or moist air is violent and may be explosive.

See related METAL HYDRIDES

0074. Aluminium hydroxide

[21645-51-2] **AlH_3O_3**

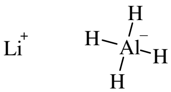


Chlorinated rubber

See CHLORINATED RUBBER: Metal oxides or hydroxides

0075. Lithium tetrahydroaluminate (Lithium aluminium hydride)

[16853-85-3] **AlH_4Li**



HCS 1980, 593; *RSC Lab. Hazard Data Sheet No. 5*, 1982

1. Augustine, 1968, 12
2. Gaylord, 1956, 37
3. Sakaliene, A. *et al., Chem. Abs.*, 1970, **73**, 19115
4. *MCA Case History No. 1832*
5. Walker, E. R. H., *Chem. Soc. Rev.*, 1976, **5**, 36
6. Brendel, G., *Chem. Eng. News*, 1979, **57**(36), 5
7. Anon., *Lab. Haz. Bull.*, 1985, (12), item 852
8. Green, M. L. H., private comm., 1986
9. Schatzschneider, U., Internet, 1996

Care is necessary in handling this powerful reducant, which may ignite if lumps are pulverised with a pestle and mortar, even in a dry box [1]. An actual explosion destroying the mortar, has been claimed as the result of attempting to grind down large pellets, though contributory factors seem probable [9]. A rubber mallet is recommended for breaking up lumps [2]. The explosive thermal decomposition of the aluminate at 150—170°C is due to its interaction with partially hydrolysed decomposition products [3]. A spilled mixture with ether ignited after the ether evaporated [4]. Sodium bis(2-methoxyethoxy)dihydroaluminate, which is of similar reducing capability to lithium tetrahydroaluminate, is safer in that it does not ignite in moist air or oxygen and is stable at 200°C [5]. A detailed comment on the latter states that the commercial (crystalline) lithium compound is not pyrophoric, even in contact with moist air of high humidity [6]. An attempt to decontaminate a polythene bag dusted with residual lithium tetrahydroaluminate by immersion in ethyl acetate caused a fire. Two alternative methods are proposed, one for light coatings of dust, which should be immersed completely in a large volume of water behind screens until reaction ceases. The other method for larger amounts involves suspension of the residue in an inert solvent (light petroleum—*flammable*), and dropwise treatment with ethyl acetate until reaction ceases. After standing, the treatment is repeated with ethanol, and then water [7]. Following the investigation of a laboratory explosion, precautions essential for the safe use of lithium aluminium hydride (LAH) have been defined [8]. The measures given below are to prevent overheating of the hydride and its dissociation to finely divided aluminium, which can then undergo thermite-like reactions with compounds or solvents containing combined oxygen or halogen.

a. All apparatus and reactants should be perfectly dry, and reactions should be run rigorously under nitrogen, with the reaction temperature below 60°C at all times.

b. Order of addition is important. Always first add the hydride to the solvent in the nitrogen-purged apparatus, before adding the other reactant last.

c. The hydride should never be allowed to form a crust above the level of the liquid or to settle to the bottom, so efficient but gentle stirring is absolutely essential.

d. To prevent local overheating of the reaction vessel, heating mantles should never be used: always use an oil bath as heat source.

e. After reduction has been effected, destroy excess LAH by slow and careful addition of dry ethyl acetate (preferably diluted with inert solvent), again under

nitrogen and keeping the temperature below 60°C. All LAH reactions should be carried out behind suitable protective screens.
See Ethyl acetate, below

Alkyl benzoates

1. Tados, W. *et al., J. Chem. Soc.*, 1954, 2353
2. Field, B. O. *et al., J. Chem. Soc.*, 1955, 1111

Application of a method for reducing benzaldehydes to the corresponding alcohols with a fourfold excess of the aluminate [1] to alkyl benzoates proved to be difficult to control and frequently dangerous [2].

Bis(2-methoxyethyl) ether

1. Watson, A. R., *Chem. & Ind.*, 1964, 665
2. Adams, R. M., *Chem. Eng. News*, 1953, **31**, 2334
3. Barbaras, G. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 877
4. *MCA Case History No. 1494*
5. Author's comment, 1987

The peroxide-free ether, being dried by distillation at 162°C under inert atmosphere at ambient pressure, exploded violently when the heating bath temperature had been raised to 200°C towards the end of distillation. This was attributed to local overheating of an insulating crust of hydride in contact with oxygen-containing organic material [1]. Two previous explosions were attributed to peroxides [2] and the high solubility of carbon dioxide in such ethers [3]. Stirring during distillation would probably prevent crust formation. Alternatively, drying could be effected with a column of molecular sieve or activated alumina. During distillation of the solvent from the aluminate at 100°C at ambient pressure, the flask broke and the contents ignited explosively. The aluminate decomposes at 125—135°C [4]. It seems probable that at least some of these incidents are better explained as arising from formation of finely divided aluminium from overheating of the hydride, and a thermite-like reaction with the oxygen-containing solvent [5]. See initial reference 8 above for precautions to avoid this.
See Aluminium hydride: Carbon dioxide

Boron trifluoride diethyl etherate

1. Scott, R. B., *Chem. Eng. News*, 1967, **45**(28), 7; **45**(21), 51
2. Shapiro, I. *et al., J. Amer. Chem. Soc.*, 1952, **74**, 90

Use of lumps of the solid aluminate, rather than its ethereal solution, and of peroxide-containing etherate [1], rather than the peroxide-free material specified [2], caused an explosion during the attempted preparation of diborane.

Dibenzoyl peroxide MRH 4.39/85
See Dibenzoyl peroxide: Lithium tetrahydroaluminate

3,5-Dibromocyclopentene
Johnson, C. R. *et al., Tetrahedron Lett.*, 1964, **45**, 3327
Preparation of the 4-bromo compound by partial debromination of crude 3,5-dibromocyclopentene by addition of its ethereal solution to the aluminate in ice-cold ether is

hazardous. Explosions have occurred on 2 occasions about 1 h after addition of dibromide.

1,2-Dimethoxyethane

1. *MCA Case History No. 1182*
2. Hoffman, K. A. *et al., Org. Synth.*, 1968, **48, 62**

The finely powdered aluminate was charged through a funnel into a nitrogen-purged flask. When the solvent was added through the same funnel, ignition occurred, possibly due to local absence of purge gas in the funnel caused by turbulence [1]. Distillation of the solvent from the solid must not be taken to dryness, to avoid explosive decomposition of the residual aluminate [2].

Dioxane

1. Anon., private comm., 1976
2. Author's comments, 1987

Dioxane was purified by distillation from the complex hydride in a glass still, and when the residue was cooling down, a severe explosion and fire occurred [1]. This may have been caused by ingress of air into the cooling dioxane vapour (flammability limits 2—22%), then subsequent oxidative heating of finely divided hydride deposited on the upper parts of the still on contact with air to above the rather low autoignition temperature of dioxane (180°C). Nitrogen purging will render the operation safe. However, the alternative explanation of a thermite-like reaction with dioxane, arising from overheating of the hydride (initial reference 8 above) may be equally probable. If this were the case, nitrogen purging alone would not necessarily render the operation safe [2]. See reference 8 above for preventive measures.

Ethyl acetate

1. Bessant, K. H. C., *Chem. & Ind.*, 1957, 432
2. Yardley, J. T., *Chem. & Ind.*, 433

Following a reductive dechlorination in ether, a violent explosion occurred when ethyl acetate was added to decompose excess aluminate [1]. Ignition was attributed to the strongly exothermic reaction occurring when undiluted (and reducible) ethyl acetate contacts the solid aluminate. Addition of a solution of ethyl acetate in inert solvent or of a moist unreactive solvent to destroy excess reagent is preferable [2].
See reference 1—7, above

Fluoroamides

1. Karo. W., *Chem. Eng. News*, 1955, **33**, 1368
2. Reid, T. S. *et al., Chem. Eng. News*, 1951, **29**, 3042

The reduction of amides of fluorocarboxylic acids with the tetrahydroaluminate appears generally hazardous at all stages. During reduction of *N*-ethylheptafluorobutyramide in ether, violent and prolonged gas evolution caused a fire. Towards the end of reduction of trifluoroacetamide in ether, solid separated and stopped the stirrer. Attempts to restart the stirrer by hand caused a violent explosion [1]. During decomposition by water of the reaction complex formed by interaction with tetrafluorsuccinamide in ether, a violent explosion occurred. Reaction complexes similarly obtained from trifluoroacetic acid, heptafluorobutyramide and octafluoroadipamide also showed instability, decomposing when heated. General barricading of all reductions of fluorocompounds with lithium tetrahydroaluminate is recommended [2].

See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS

Hydrogen peroxide

See Hydrogen peroxide: Lithium tetrahydroaluminate

Nitrogen

1. Metts, L., *Chem. Eng. News*, 1981, **59**(31), 3
2. Grossman, M. I., *Chem. Eng. News*, 1981, **59**(41), 57
3. Deberitz, J., *Chem. Eng. News*, 1982, **60**(11), 3

The incident which originally described the glowing residue from combustion in air of a pellet of hydride as being able to burn under nitrogen [1] was later interpreted as ‘ignition of the hydride in a nitrogen atmosphere’ [2]. It is later stressed that the hydride itself does not react directly with nitrogen under any foreseeable conditions of normal use. After combustion, the residue of hot aluminium and lithium metals would be expected to react with nitrogen [3].

Nitromethane

See Nitromethane: Lithium tetrahydroaluminate

Pyridine

Augustine, 1968, 22—23

Addition of the aluminate (0.5 g) to pyridine (50 ml) must be effected very slowly with cooling. Addition of 1 g portions may cause a highly exothermic reaction.

1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide

See 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide: Lithium tetrahydroaluminate

Tetrahydrofuran

Moffett, R. B., *Chem. Eng. News*, 1954, **32**, 4328

The solvent had been dried over the aluminate and then stored over calcium hydride for 2 years ‘to prevent peroxide formation’. Subsequent addition of more aluminate caused a strong exotherm and ignition of liberated hydrogen. Calcium hydride does not prevent peroxide formation in solvents.

See other PEROXIDATION INCIDENTS

Water

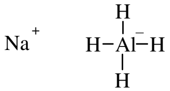
1. Leleu, *Cahiers*, 1977, (86), 100
2. Anon., *Fire Prevention*, 1986, (191), 43

Interaction is very vigorous, and with limited water, incandescent [1]. An account of a serious fire caused by inadvertent addition of lithal to water [2]. In the editor’s experience ignition of evolved hydrogen will occur with quantities as slight as 200 mg.

See other COMPLEX HYDRIDES, GAS EVOLUTION INCIDENTS

0076. Sodium tetrahydroaluminate (Sodium aluminium hydride)

[13770-96-2] **AlH_4Na**



Tetrahydrofuran

Del Giudia, F. P. *et al., Chem. Eng. News*, 1961, **39**(40), 57

During synthesis from its elements in tetrahydrofuran, a violent explosion occurred when absorption of hydrogen had stopped. This was attributed to deposition of solid above the liquid level, overheating and reaction with solvent to give butoxyaluminium hydrides. Vigorous stirring and avoiding overheating are essential.

Water

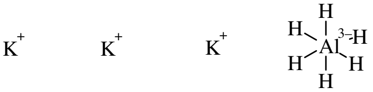
Gibson, 1969, 85

It may ignite and explode in contact with water.

See other COMPLEX HYDRIDES

0077. Potassium hexahydroaluminate(3—)

[17083-63-5] **AlH_6K_3**



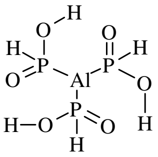
Ashby, E. C., *Chem. Eng. News*, 1969, **47**(1), 9

A 20 g sample, prepared and stored in a dry box for several months, developed a thin crust of oxidation/hydrolysis products. When the crust was disturbed, a violent explosion occurred, later estimated as equivalent to 230 g TNT. A weaker explosion was observed with potassium tetrahydroaluminate. The effect was attributed to superoxidation of traces of metallic potassium, and subsequent interaction of the hexahydroaluminate and superoxide after frictional initiation. Precautions advised include use of freshly prepared material, minimal storage in a dry diluent under an inert atmosphere and destruction of solid residues. Potassium hydrides and caesium hexahydroaluminate may behave similarly, as caesium also superoxidises in air.

See other COMPLEX HYDRIDES

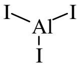
0078. Aluminium phosphinate

[24704-64-1] **$AlH_6O_6P_3$**



Mellor, 1971, Vol. 8, Suppl. 3, 623
It decomposes at around 220°C liberating spontaneously flammable phosphine.
See other METAL PHOSPHINATES

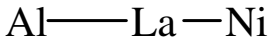
0079. Aluminium iodide
[7784-23-8] **AlI_3**



Alone, or Water
Bailar, 1973, Vol. 1, 1023
It reacts violently with water, and on heating produces flammable vapour which may explode if mixed with air and ignited.

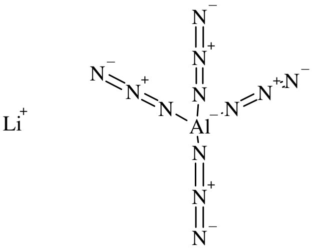
Aluminium, Carbon oxides
See Aluminium: Aluminium halides, Carbon oxides
See other METAL HALIDES

0080. Aluminium—lanthanum—nickel alloy
[66459-02-7] **$AlLaNi_4$**



Mendelsohn, M. H. *et al., Inorg. Synth.*, 1083, **22**, 99
The alloy powder (used in hydrogen-storage systems) may ocasionally be pyrophoric after hydriding—dehydriding operations, igniting when placed on a combustible surface (e.g. weighing paper).
See other ALLOYS, PYROPHORIC ALLOYS

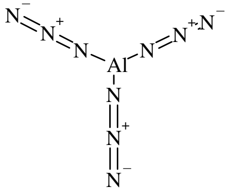
0081. Lithium tetraazidoaluminate
[67849-02-9] **$AlLiN_{12}$**



Mellor, 1967, Vol. 8, Suppl. 2, 2
A shock-sensitive explosive.
See other HIGH-NITROGEN COMPOUNDS
See related METAL AZIDES

0082. Aluminium azide

[39108-14-0] **AlN_9**



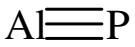
Brauer, 1963, Vol. 1, 829

Containing 82.3% of nitrogen, it may be detonated by shock.

See other HIGH-NITROGEN COMPOUNDS, METAL AZIDES

0083. Aluminium phosphide

[20859-73-8] **AlP**



HCS 1980, 133

Mineral acids

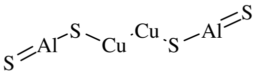
1. Wang. C. C. *et al., J. Inorg. Nucl. Chem.*, 1963, **25**, 327
2. Mellor, 1971, Vol. 8, Suppl. 3, 306
3. www.chemsafety.gov/circ., US Chem. Safety Board Incident No. 2002-5492

Evolution of phosphine is slow in contact with water or alkali, but explosively violent in contact with dilute mineral acids [1]. However, reports of violent interaction with concentrated or dilute hydrochloric acid, and of explosive reaction with 1:1 aqua regia, have been questioned [2]. A report is given of an explosion when fumigant containing the phosphide, discarded to a waste-bin, was damped by rain [3].

See other GAS EVOLUTION INCIDENTS, METAL NON-METALLIDES

0084. Aluminium copper(I) sulfide

[12003-23-5] **$Al_2Cu_2S_4$**



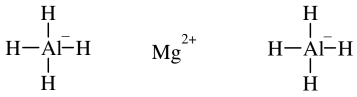
Preparative hazard

See Aluminium: Copper, Sulfur

See other METAL SULFIDES

0085. Magnesium tetrahydroaluminate

[17300-62-8] **Al_2H_8Mg**



$$H-\overset{H}{\underset{H}{Al^-}}-H \qquad Mg^{2+} \qquad H-\overset{H}{\underset{H}{Al^-}}-H$$

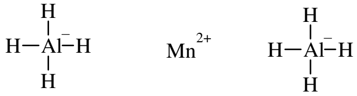
Gaylord, 1956, 25

It is similar to the lithium salt.

See other COMPLEX HYDRIDES

0086. Manganese(II) tetrahydroaluminate

[65776-39-8] **Al_2H_8Mn**



$$H-\overset{H}{\underset{H}{Al^-}}-H \qquad Mn^{2+} \qquad H-\overset{H}{\underset{H}{Al^-}}-H$$

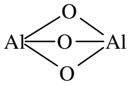
Aubry, J. *et al., Compt. rend.*, 1954, **238**, 2535

The unstable hydride decomposes at —80°C and ignites in contact with air.

See other COMPLEX HYDRIDES

0087. Aluminium oxide ('Alumina')

[1344-28-1] **Al_2O_3**



HCS 1980, 132

Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Ethylene oxide

See Ethylene oxide: Contaminants

Halocarbons, Heavy metals

Burbidge, B. W., unpublished information, 1976

It is known that alumina is chlorinated exothermically at above 200°C by contact with halocarbon vapours, and hydrogen chloride, phosgene etc. are produced. It has now been found that a Co/Mo—alumina catalyst will generate a substantial exotherm in contact with vapour of carbon tetrachloride or 1,1,1-trichloroethane at ambient temperature in presence of air. In absence of air, the effect is less intense. Two successive phases appear to be involved: first, adsorption raises the temperature of the alumina; then reaction, presumably metal-catalysed, sets in with a further exotherm.

Oxygen difluoride

See Oxygen difluoride: Adsorbents

Sodium nitrate

See Sodium nitrate: Aluminium, etc.

Vinyl acetate

See Vinyl acetate: Desiccants

See other METAL OXIDES

0088. Dialuminium octavanadium tridecasilicide

[ ] **$Al_2Si_{13}V_8$**

Complex Structure

Hydrofluoric acid

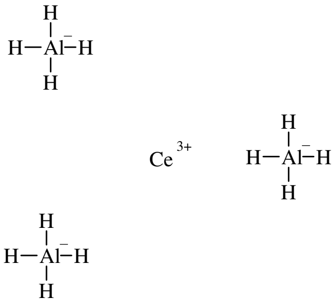
Sidgwick, 1950, 833

The silicide reacts violently with the aqueous acid.

See other METAL NON-METALLIDES

0089. Cerium(III) tetrahydroaluminate

[65579-06-8] **Al_3CeH_{12}**



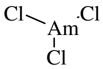
Aubry, J. *et al., Compt. rend.*, 1954, **238**, 2535

The unstable hydride decomposes at —80°C, and ignites in contact with air.

See other COMPLEX HYDRIDES

0090. Americium trichloride

[13464-46-5] **$AmCl_3$**



MCA Case History No. 1105

A multi-wall shipping container, holding 400 ml of a solution of americium chloride in a polythene bottle and sealed for over 3 months, exploded. The reason could have been a slow pressure build-up of radiolysis products. Venting and other precautions are recommended.

See Radon: Water
See other GAS EVOLUTION INCIDENTS, METAL HALIDES

0091. Argon
[7440-37-1] **Ar**

Ar

Liquid nitrogen

1. Baker, K., *Chem. Brit.*, 1979, **15**, 65
2. Janiaut, H., *Actual Chim.*, 1986, (1—2), 59—61

The presence of argon in apparatus cooled by liquid nitrogen can lead to hazardous situations with the possibility of explosion. This is because argon solidifies at —189°C and has so low a vapour pressure at —196°C that the solid may survive exposure to high vacuum for a considerable period, and subsequently evaporate on warming with generation of high pressure. Use of solid CO_2—solvent baths is recommended for argon [1]. A phenylhydrazone was vacuum-degassed and frozen in liquid nitrogen, probably during freeze-drying. Vacuum was broken by slow admission of argon (some of which would condense and solidify), and the flask, still under liquid nitrogen, was sealed. During subsequent warming to ambient temperature, the flask exploded violently from internal gas pressure [2].
See other GAS EVOLUTION INCIDENTS

Magnesium perchlorate
See Magnesium perchlorate: Argon
See other NON-METALS

0092. Arsenic
[7440-38-2] **As**

As

NSC 499, 1979 (As and its inorganic compounds); *RSC Lab. Hazard Data Sheet No. 62*, 1987 (As and compounds)

Müller, W. J., *Z. Angew. Chem.*, 1914, **27**, 338
An explosive variety (or compound) of arsenic was produced as a surface layer on the exposed iron surfaces of a corroded lead-lined vessel which contained 35% sulfuric acid with a high arsenic content. It exploded on friction or ignition, and contained no hydrogen, but variable small amount of iron and lead. It may have been analogous to explosive antimony.

Bromine azide
See Bromine azide

Halogens or Interhalogens

1. Mellor, 1946, Vol. 2, 92
2. Mellor, 1956, Vol. 2, Suppl. 1, 379

The finely powdered element inflames in gaseous chlorine or liquid chlorine at —33°C [1]. The latter is doubtful [2].

See Bromine pentafluoride: Acids, etc.
Bromine trifluoride: Halogens, etc.
Chlorine trifluoride: Metals, etc.
Iodine pentafluoride: Metals, etc.

Metals

Mellor, 1940, Vol. 4, 485—486; 1942, Vol. 15, 629; 1937, Vol. 16, 161

Palladium or zinc and arsenic react on heating with evolution of light and heat, and platinum with vivid incandescence.

See Aluminium: Antimony, etc.

Nitrogen trichloride

See Nitrogen trichloride: Initiators

Oxidants

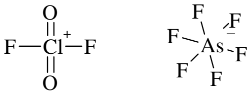
Dichlorine oxide: Oxidisable materials
Nitrosyl fluoride: Metals, etc.
Potassium dioxide: Metals
Potassium permanganate: Antimony, etc.
Silver nitrate:Arsenic
Sodium peroxide: Non-metals
See Chromium trioxide: Arsenic

Rubidium acetylide

See Rubidium acetylide: Non-metals
See other NON-METALS

0093. Difluoroperchloryl hexafluoroarsenate

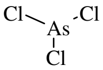
[39003-82-2] **$AsClF_8O_2$**



See entry DIFLUOROPERCHLORYL SALTS

0094. Arsenic trichloride

[7784-34-1] **$AsCl_3$**



HCS 1980, 165

Aluminium

See Aluminium: Non-metal halides

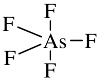
Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

See other NON-METAL HALIDES

0095a. Arsenic pentafluoride

[7784-36-3] **AsF_5**



Benzene, Potassium methoxide

Kolditz, L. *et al., Z. Anorg. Chem.*, 1965, **341**, 88—92

Interaction of the pentafluoride and methoxide proceeded smoothly in trichlorotrifluoroethane at 30—40°C, whereas in benzene as solvent repeated explosions occurred.

1,3-Butadiyne

See 1,3-Butadiyne: Arsenic pentafluoride

Krypton difluoride

See Krypton difluoride: Arsenic pentafluoride

See other NON-METAL HALIDES

0095b. Pentazonium hexafluorarsenate (Nitrogen ion (N_5^+) hexafluoroarsenate)

[236412-65-0] **AsF_6N_5**

$$N{\equiv}N^+{—}N^-{—}N^+{\equiv}N\ AsF_6{}^-$$

1. Anon., *Chem. Brit.*, 1999, **35**(4), 18
2. Christe, K.O. *et al., Angew. Chem. (Int.)*, 1999, **38**, 2004
3. Dagani, R., *Chem. Eng. News*, 2000, **78**(33), 41
4. Vij, A. *et al., J. Amer. Chem. Soc.*, 2001, **123**(26), 6308
5. Dixon, D. A. *et al., J. Amer. Chem. Soc.*, 2004, **126**(3), 834

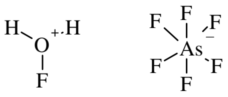
The above compound, exploding during mass spectrometry and on contact with water, is marginally stable at room temperature. It is an oxidant also exploding on contact with hydrogen or organic material and is estimated to have a heat of formation of above 6 kJ/g. It should be handled only on very small scale [1,2]. The hexafluoroantimonate and undecafluorodiantimonate are considerably more stable [3,4]. An attempt to prepare pentazonium azide from the hexafluoroantimonate revealed only that reaction between this and alkali azides is violent to explosive. Subsequent computation discounted the possibility of a stable azide or pentazolide (which would have been new allotropes of nitrogen) [5].

See also HIGH NITROGEN COMPOUNDS

0096. Fluorokrypton hexafluoroarsenate
[50859-36-4] AsF_7Kr

See Krypton difluoride: Arsenic pentafluoride
See XENON COMPOUNDS

0097. Monofluoroxonium hexafluoroarsenate
[ ] AsF_7H_2O



Minkwitz, R. *et al., Angew. Chem. Int.,* 1990, **29**(6), 689
The above salt is a powerful oxidant, reacting explosively with methanol even at —40°C. The antimonate is similar.
See other OXIDANTS

0098. Difluoroammonium hexafluoroarsenate
[56533-30-3] AsF_8H_2N

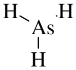
Christe, K. O., *Inorg. Chem.*, 1975, **14**, 2821—2824
Solutions of this and the hexafluoroantimonate salt in hydrogen fluoride, kept for extended periods between —50 and +50°C, burst the Kel-F or Teflon FEP containers. This was attributed to excess pressure of hydrogen fluoride and nitrogen arising from decomposition of the salts. The variable rates of decomposition indicated catalysis by trace impurities. The salts also decompose exothermally after a short period at ambient temperature.
See other GAS EVOLUTION INCIDENTS, *N*-HALOGEN COMPOUNDS

0099. Trifluoroselenium hexafluoroarsenate
[59544-89-7] AsF_9Se

Water
Bartlett, N. *et al., J. Chem. Soc.*, 1956, 3423
Violent interaction.
See related NON-METAL HALIDES

†0100. Arsine

[7784-42-1] **AsH_3**



HCS 1980, 167 (cylinders); *RSC Lab. Hazard Data Sheet No. 51*, 1986

1. Rüst, 1948, 301
2. Kayser, J. C., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 289—315, Heidelberg, ISSA, 1987

Arsine is strongly endothermic, and can be detonated by suitably powerful initiation [1]. The potential hazards involved in setting up and operating a plant for manufacture of arsine for semi-conductor use have been studied [2].

Chlorine

See Chlorine: Non-metal hydrides

Nitric acid

See Nitric acid: Non-metal hydrides

See other ENDOTHERMIC COMPOUNDS, NON-METAL HYDRIDES

0101. Arsine—boron tribromide

[65313-32-8] **$AsH_3.BBr_3$**

Oxidants

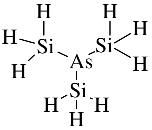
1. Stock, A., *Ber.*, 1901, **34**, 949
2. Mellor, 1939, Vol. 9, 57

Unlike arsine, the complex ignites on exposure to air or oxygen, even at below 0°C [1]. It is violently oxidised by nitric acid [2].

See related NON-METAL HALIDES, NON-METAL HYDRIDES

0102. Trisilylarsine

[15110-34-6] **AsH_9Si_3**



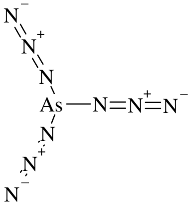
Leleu, *Cahiers*, 1977, (88), 363

Ignites in air.

See related SILANES

0103a. Triazidoarsine (Arsenous triazide)

[167771-41-7] **AsN_9**

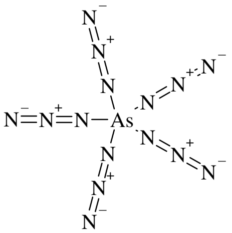


See entry Tetraazidoarsonium hexafluoroarsenate

See other NON-METAL AZIDES

0103b. Arsenic pentaazide

[364329-89-5] (ammine) **AsN_{15}**



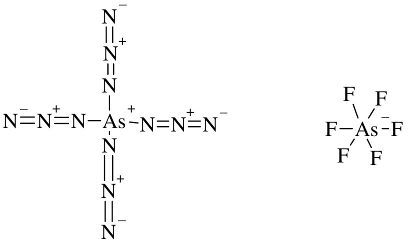
Klapötke, T. *et al., J. Fluor. Chem.*, 2001, **109**(2), 151

It is possible to synthesise this species as complexes with one equivalent of a variety of amines, from ammonia to quinoline. The complexes are storable at room temperature but highly explosive on heating or under mechanical shock. The antimony analogues are similar.

NON-METAL AZIDES

0104. Tetraazidoarsonium hexafluoroarsenate

[171565-26-7] **$As_2F_6N_{12}$**

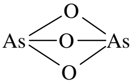


1. Tornieporth-Oetting, I. C. *et al., Angewand. Chem. (Int.)*, 1995, **34**(5), 511
2. Klapoetke, T. M. *et al., J. Chem. Soc., Dalton Trans.*, 1995, (20), 3365

As might be expected, it is violently explosive, as is the precursor triazidoarsine; any other salts of this hitherto unknown arsonium ion may also prove so.

See other NON-METAL AZIDES

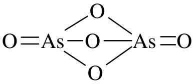
0105. Arsenic trioxide
[1327-53-3] **As_2O_3**



(*MCA SD-60*, 1956); *HCS 1980*, 166

Various reagents
See Chlorine trifluoride: Metals, etc.
Hydrogen fluoride: Oxides
Sodium nitrate: Arsenic trioxide, etc.
Zinc: Arsenic trioxide
See other NON-METAL OXIDES

0106. Arsenic pentaoxide
[1303-28-2] **As_2O_5**



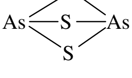
Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.
See other NON-METAL OXIDES

0107. Platinum diarsenide
[12044-52-9] **As_2Pt**

$As^{3-}\ Pt^{6+}\ As^{3-}$

Preparative hazard
See Platinum: Arsenic
See other METAL NON-METALLIDES

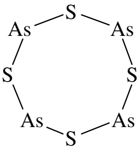
0108. Arsenic trisulfide
[1303-33-9] **As_2S_3**



Oxidants
Potassium chlorate: Arsenic trisulfide
See Chloric acid: Metal sulfides
See other NON-METAL SULFIDES

0109. Tetraarsenic tetrasulfide

[12279-90-2] **As_4S_4**



Oxidants

Chlorine: Sulfides

Potassium nitrate: Metal sulfides

See Chloric acid: Metal sulfides

See other NON-METAL SULFIDES

0110. Gold

[7440-57-5] **Au**

Au

Fisher, G. *Chem. Brit.*, 2003, **39**(12), 12

Warning is given against preparing supported gold catalysts by reacting gold salts with ammmonia compounds. This has led to explosive ‘fulminating gold’ as intermediate and ‘incidents’.

Analytical hazard

See Gold(III) chloride, next below

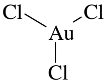
Hydrogen peroxide

See Hydrogen peroxide: Metals

See other METALS

0111. Gold(III) chloride

[13453-07-1] **$AuCl_3$**



Ammonia and derivatives

1. Mellor, 1941, Vol. 3, 582—583
2. Sidgwick, 1950, 178
3. *491M*, 1975, 194

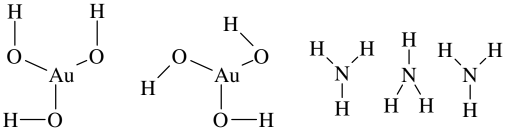
Action of ammonia or ammonium salts on gold chloride, oxide or other salts under a wide variety of conditions gives explosive or ‘fulminating’ gold [1]. Of uncertain composition but containing Au—N bonds, this is a heat-, friction- and impact-sensitive explosive when dry, similar to the related mercury and silver compounds [2]. In an attempt to precipitate finely divided gold from its solution in aqua regia

(effectively gold chloride solution), ammonia solution was added instead of ammonium oxalate. The precipitated 'gold' subsequently exploded when heated in a furnace with other metals to prepare an alloy [3].
See FULMINATING GOLD

Potassium cyanate
Selig, W. S., *Microchem. J.*, 1990, **41**(3), 386
A precipitate, explosive when touched after drying, which appeared from a neutralised solution stood overnight with a large excess of potassium cyanate, was described as a fulminate. This is unlikely, though fulminating gold is probable, cyanate hydrolysing to release ammonia (see above). Existence of explosive cyanate complexes is also conceivable.
See other GOLD COMPOUNDS, METAL HALIDES

0112. Gold(III) hydroxide—ammonia

[ ] **$2AuH_3O_3.3H_3N$**

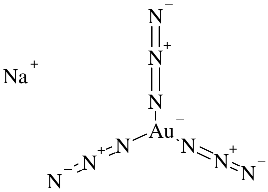


1. Sorbe, 1958, 63
2. Ephraim, 1939, 463

Explosive gold, formed from the hydroxide and ammonia, is formulated as above [1]. Dry heating forms the equally explosive Au_2O_3 . $3NH_3$, then $3Au_2O$. $4NH_3$, while heating with water forms the more explosive Au_2O_3 . $2NH_3$. Later authors hold that fulminating gold has Au-N bonds.
See FULMINATING GOLD
See other GOLD COMPOUNDS

0113a. Sodium triazidoaurate(?)

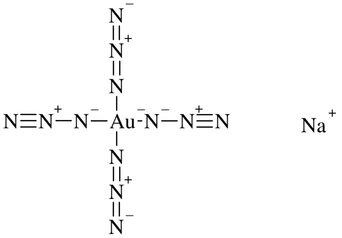
[ ] **AuN_9Na**



Rodgers, G. T., *J. Inorg. Nucl. Chem.*, 1958, **5**, 339—340
The material (of unknown structure, analysing as $Au_{1.5}N_9Na$ and possibly the impure title compound) explodes at 130°C.
See other GOLD COMPOUNDS, METAL AZIDES

0113b. Sodium tetraazidoaurate

[62432-36-3] **$AuN_{12}Na$**



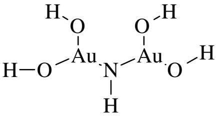
Wehlan, M. *et al., J. Organomet. Chem.*, 2000, **613**(2), 159

This salt may explode even in concentrated aqueous solution.

See other GOLD COMPOUNDS, METAL AZIDES, *N*-METAL DERIVATIVES

0114. Bis(dihydroxygold)imide

[ ] **$Au_2H_5NO_4$**



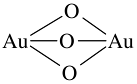
Mellor, 1940, Vol. 8, 259

An explosive compound.

See other GOLD COMPOUNDS, *N*-METAL DERIVATIVES

0115. Gold(III) oxide

[1303-58-8] **Au_2O_3**



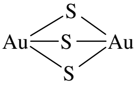
Ammonium salts

See Gold(III) chloride: Ammonia, etc.

See other ENDOTHERMIC COMPOUNDS, GOLD COMPOUNDS

0116. Gold(III) sulfide

[1303-61-3] **Au_2S_3**



Silver oxide

See Silver(I) oxide: Metal sulfides

See other GOLD COMPOUNDS, METAL SULFIDES

0117. Gold(I) nitride—ammonia

[ ] **$Au_2N_3.H_3N$**

$Au_2N_3.NH_3$

Raschig, F., *Ann.*, 1886, **235**, 349

An explosive compound, probably present in fulminating gold, produced from action of ammonia on gold(I) oxide.

See FULMINATING GOLD

See other GOLD COMPOUNDS, *N*-METAL DERIVATIVES

0118. Gold(III) nitride trihydrate

[ ] **$Au_3N_2.3H_2O$**

$Au_3N_2.3H_2O$ or $(HOAu)_3N.NH_3$

Mellor, 1940, Vol. 8, 101

Very explosive when dry.

See other GOLD COMPOUNDS, *N*-METAL DERIVATIVES

0119. Boron

[7440-42-8] **B**

B

Bailar, 1973, Vol. 1, 692

Many of the previously described violent reactions of boron with a variety of reagents are ascribed to the use of impure or uncharacterised ‘boron’. The general impression of the reactivity of pure boron, even when finely divided, is one of extreme inertness, except to highly oxidising agents at high temperatures.

Ammonia

Mellor, 1940, Vol. 8, 109

Boron incandesces when heated in dry ammonia, hydrogen being evolved.

Dichromates, Silicon

Howlett, S. *et al., Thermochim. Acta*, 1974, **9**, 213—216

The mechanism of ignition and combustion of pyrotechnic mixtures of boron with potassium dichromate and/or sodium dichromate in presence or absence of silicon are discussed.

Halogens or Interhalogens

1. Mellor, 1941, Vol. 2, 92
2. Bailar, 1973, Vol. 1, 690—691

Boron ignites in gaseous chlorine or fluorine at ambient temperature, attaining incandescence in fluorine [1]. Powdered boron reacts spontaneously with the halogens from fluorine to iodine at 20, 400, 600 and 700°C respectively [2].

See Bromine trifluoride: Halogens, etc.
Bromine pentafluoride: Acids, etc.
Chlorine trifluoride: Boron-containing materials
Iodine pentafluoride: Metals, etc.

Metals
Mellor, 1946, Vol. 3, 389; Vol. 5, 15
Explosive interaction when boron and lead fluoride or silver fluoride are ground together at ambient temperature.

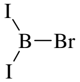
Oxidants
See Halogens or Interhalogens, above
Calcium chromate: Boron
Dinitrogen oxide: Boron
Lead(II) oxide: Non-metals
Lead(IV) oxide: Non-metals
Nitric acid: Non-metals
Nitrogen oxide: Non-metals
Nitrosyl fluoride: Metals, etc.
Nitryl fluoride: Non-metals
Oxygen difluoride: Non-metals
Potassium nitrate: Non-metals
Potassium nitrite: Boron
Silver difluoride: Boron, etc.
Sodium peroxide: Non-metals

Rubidium acetylide
See Rubidium acetylide: Non-metals

Water
1. Bailar, 1973, Vol. 1, 691
2. Shidlovskii, A. A., *Chem. Abs.*, 1963, **59**, 11178

Interaction of powdered boron and steam may become violent at red heat [1]. The highly exothermic reactions with water might become combustive or explosive processes at sufficiently high temperatures and pressures [2].
See other NON-METALS

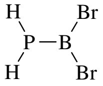
0120. Boron bromide diiodide
[14355-21-6] **$BBrI_2$**



Water
Mellor, 1946, Vol. 5, 136
Interaction is violent, as for the tribromide or triiodide.
See other NON-METAL HALIDES

0121. Dibromoborylphosphine

[30641-57-7] (polymeric form) **BBr_2H_2P**



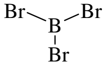
491M, 1975, 146

Ignites in air.

See related NON-METAL HALIDES, NON-METAL HYDRIDES

0122. Boron tribromide

[10294-33-4] **BBr_3**



Sodium

See Sodium: Non-metal halides (reference 7)

Tungsten trioxide

Levason, W. *et al., J. Chem. Soc., Dalton Trans.*, 1981, 2501—2507

Tungsten oxide tetrabromide was prepared by condensing a little of the bromide onto the oxide at —196°C, then allowing slow warming by immersion of the container in an ice bath. Omission of the ice bath or use of large amounts of bromide may lead to explosions.

Water

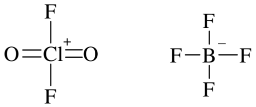
1. *BCISC Quart. Safety Summ.*, 1966, **37**, 22
2. Anon., *Lab. Pract.*, 1966, **15**, 797

Boron halides react violently with water, and particularly if there is a deficiency of water, a violent explosion may result. It is therefore highly dangerous to wash glass ampoules of boron tribromide with water under any circumstances. Following a serious accident, experiment showed that an ampoule of boron tribromide, when deliberately broken under water, caused a violent explosion, possibly a detonation. Only dry non-polar solvents should be used for cleaning or cooling purposes [1]. Small quantities of boron tribromide may be destroyed by cautious addition to a large volume of water, or water containing ice [2].

See other GLASS INCIDENTS, NON-METAL HALIDES

0123. Difluoroperchloryl tetrafluoroborate

[38682-34-7] **$BClF_6O_2$**

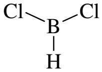


$\mathrm{O{=}\overset{+}{Cl}F_2{=}O \quad F{-}\overset{-}{B}F_2{-}F}$

See entry DIFLUOROPERCHLORYL SALTS

0124. Dichloroborane

[10325-39-0] **BCl_2H**



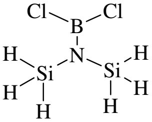
Bailar, 1973, Vol. 1, 742

Ignites in air.

See related NON-METAL HALIDES

0125. Dichlorodisilylaminoborane

[25573-61-9] **$BCl_2H_6NSi_2$**



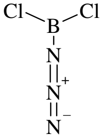
491M, 1975, 149

Ignites in air.

See related NON-METAL HALIDES, NON-METAL HYDRIDES

0126. Boron azide dichloride

[ ] **BCl_2N_3**



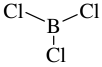
1. Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 27
2. Paetzold, P. I., *Z. Anorg. Chem.*, 1963, **326**, 47

A hard crust of sublimed material exploded when crushed with a spatula [1]. Explosions on sublimation or during solvent removal were known previously [2].

See related NON-METAL AZIDES

0127. Boron trichloride

[10294-34-5] **BCl_3**



HCS 1980, 215 (cylinder)

Aniline

Jones, R. G., *J. Amer. Chem. Soc.*, 1939, **61**, 1378

In absence of cooling or diluent, interaction is violent.

Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Boron trichloride

Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

Methanol

Anon., *Safety Digest Univ. Safety Assoc.*, 1989, **34**, 16

On addition of boron trichloride, dropwise, to methanol an explosion and fire resulted. The academic reporter appears unaware that reaction of these was reported in 1834, and attributes the explosion to water in his methanol. Since the chloride is a gas, ability to add it dropwise is puzzling. Had a phonetic error meant PCl_3 was employed the fire would be intelligible, since phosphine would be formed as a pyrophoric byproduct.

Phosphine

Mellor, 1946, Vol. 5, 132

Interaction is energetic.

Triethylsilane

Matteson, D. S. *et al., J. Org. Chem.*, 1990, **55**, 2274

A pressure build-up, septum expulsion and combustion was experienced on mixing these reagents at —78°C.

See other NON-METAL HALIDES

0128. Dicobalt boride

[12045-01-1] **BCo_2**

Co_2B

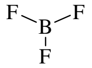
Heinzmann, S. W. *et al., J. Amer. Chem. Soc.*, 1982, **104**, 6801 (footnote 22)

The boride precipitated from sodium borohydride and cobalt(II) chloride in methanol becomes pyrophoric after vacuum drying. It can safely be stored solvent-moist.

See other METAL NON-METALLIDES, PYROPHORIC MATERIALS

0129. Boron trifluoride

[7637-07-2] **BF_3**



HCS 1980, 216 (cylinder)

Alkali metals, or Alkaline earth metals (not magnesium)

Merck Index, 1976, 175

Interaction hot causes incandescence.

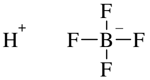
Alkyl nitrates

See Alkyl nitrates: Lewis acids

See other NON-METAL HALIDES

0130. Tetrafluoroboric acid

[16872-11-0] **BF_4H**



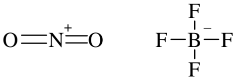
Acetic anhydride

See Acetic anhydride: Tetrafluoroboric acid

See other INORGANIC ACIDS

0131. Nitronium tetrafluoroborate

[13826-86-3] **BF_4NO_2**

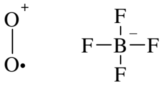


Tetrahydrothiophene-1,1-dioxide

See entry NITRATING AGENTS

0132. Dioxygenyl tetrafluoroborate

[12228-13-6] **BF_4O_2**



Organic materials

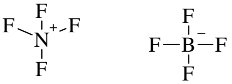
Goetschel, C. T. *et al., J. Amer. Chem. Soc.*, 1969, **91**, 4706

It is a very powerful oxidant, addition of a small particle to small samples of benzene or 2-propanol at ambient temperature causing ignition. A mixture prepared at —196°C with either methane or ethane exploded when the temperature was raised to —78°C.

See other OXIDANTS

0133. Tetrafluoroammonium tetrafluoroborate

[15640-93-4] **BF_8N**



2-Propanol

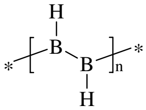
Goetschel, C. T. *et al., Inorg. Chem.*, 1972, **11**, 1700

When the fluorine used for synthesis contained traces of oxygen, the solid behaved as a powerful oxidant (causing 2-propanol to ignite on contact) and it also exploded on impact. Material prepared from oxygen-free fluorine did not show these properties, which were ascribed to the presence of traces of dioxygenyl tetrafluoroborate (above).

See other CATALYTIC IMPURITY INCIDENTS, *N*-HALOGEN COMPOUNDS

0134. Poly[borane(1)]

[13766-26-2] **$(BH)_n$**



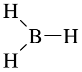
Bailar, 1973, Vol. 1, 740

Ignites in air.

See other BORANES

0135. Borane

[13283-31-3] **BH_3**



The monomeric borane is extremely endothermic (ΔH_f° +105.5 kJ/mol, 7.62 kj/g) and on formation apparently immediately dimerises to diborane (or higher boranes). It is usually stabilised as the monomer by the formation of various complexes with N, O, P or S donor molecules and many of these are available commercially.

See other BORANES, ENDOTHERMIC COMPOUNDS

0136. Borane—dimethylsulfide

[13292-87-0] **$BH_3.C_2H_6S$**

$(CH_3)_2S.BH_3$

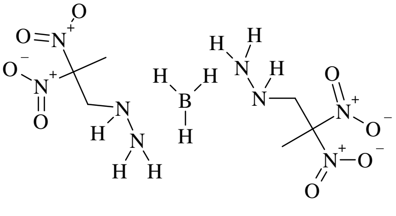
Clinton, F. L., *Chem. Eng. News*, 1992, **70**(35), 5

Bottles of this complex sometimes pressurise during ambient temperature storage. The cause, which it is hoped has now been eliminated, may be traces of thiols reacting to form hydrogen. Cold storage, careful opening and regular venting are desirable.

See other BORANES

0137. Borane—bis(2,2-dinitropropylhydrazine)

[ ] **$BH_3.2C_3H_8N_4O_4$**



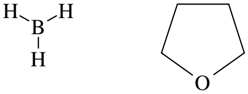
Gao, F. *et al., Youji Huaxue*, 1984, (2), 123—124 (Ch.)

It decomposes rapidly at ambient temperature and ignites or explodes within 1—2 h.

See other REDOX COMPOUNDS
See related BORANES, POLYNITROALKYL COMPOUNDS

0138. Borane—tetrahydrofuran

[14044-65-6] **$BH_3.C_4H_8O$**



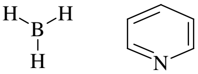
1. Bruce, M. I., *Chem. Eng. News*, 1974, **52**(41), 3
2. Hopps, H., *Chem. Eng. News*, 1974, **52**(41), 3
3. Gaines, D. F. *et al., Inorg. Chem.*, 1963, **2**, 526
4. Kollonitsch, J., *Chem. Eng. News*, 1974, **52**(47), 3
5. University of Arizona Lab. Safety Notes, 1998, (summer), 2
6. Anon., *Chem. Eng. News*, 2002, **80**(26), 7
7. am Ende, D. J. *et al., Org. Process R & D*, 2003, **7**(6), 1029

A glass bottle containing a 1M solution of the complex in THF exploded after 2 weeks in undisturbed laboratory storage out of direct sunlight at 15°C [1]. The problem of pressure build-up during storage of such commercial solutions (which are stabilised with 5 mol% of sodium tetrahydroborate) at above 0°C had been noted previously, and was attributed to presence of moisture in the original containers [2]. However, by analogy with the known generation of hydrogen in tetrahydoborate—diborane—bis(2-methoxyethyl) ether systems [3], it is postulated that the tetrahydroborate content may in fact destabilise the borane—THF reagent, with generation of hydrogen pressure in the closed bottle [4]. Storage at 0°C and opening bottles behind a screen are recommended [2]. A more recent incident involves two bottles of a 1M solution exploding while being transferred between refrigerators [5]. A drum of the complex exploded, causing several injuries and stripping the roof of the bulding in which it was stored. Other drums were found to be pressurised. The photograph does not indicate that secondary reports of detonation were justified [6]. Self-sustaining exothermic decomposition above 40°C may become violent at about 60°C; apparently the THF ring is reductively cleaved [7].

See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS
See related BORANES

0139. Borane—pyridine

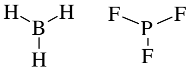
[110-51-0] **$BH_3.C_5H_5N$**



1. Brown, H. C. *et al., J. Amer. Chem. Soc.*, 1956, **78**, 5385
2. Baldwin, R. A. *et al., J. Org. Chem.*, 1961, **26**, 3550

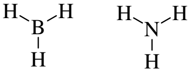
Decomposition was rapid at 120°C/7.5 mbar [1], and sometimes violent on attempted distillation at reduced pressure [2].
See related BORANES

0140. Borane—phosphorus trifluoride
[14931-39-6] **$BH_3.F_3P$**



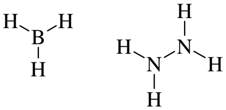
Mellor, 1971, Vol. 8, Suppl. 3, 442
The unstable gas ignites in air.
See related BORANES, NON-METAL HALIDES

0141. Borane—ammonia
[17596-45-1] **$BH_3.H_3N$**



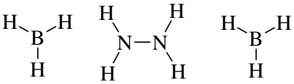
Sorbe, 1968, 56
It may explode on rapid heating.
See related BORANES

0142. Borane—hydrazine
[14931-40-9] **$BH_3.H_4N_2$**



Gunderloy, F. C., *Inorg. Synth.*, 1967, **9**, 13
It is shock-sensitive and highly flammable, like the bis(borane) adduct.
See related BORANES

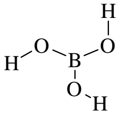
0143. Bis(borane)—hydrazine
[13730-91-1] **$(BH_3)_2.H_4N_2$**



See Borane—hydrazine
See related BORANES

0144. Boric acid

[10043-35-3] **BH_3O_3**



HCS 1980, 214

Acetic anhydride

See Acetic anhydride: Boric acid

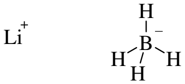
Potassium

See Potassium: Oxidants

See other INORGANIC ACIDS

0145. Lithium tetrahydroborate (Lithium borohydride)

[16949-15-8] **BH_4Li**



Water

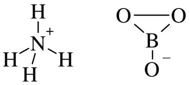
Gaylord, 1965, 22

Contact with limited amounts of water, either as liquid or that present as moisture in cellulose fibres, may cause ignition after a delay.

See other COMPLEX HYDRIDES

0146. Ammonium peroxoborate

[17097-12-0] **BH_4NO_3**



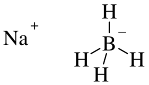
Menzel H. *et al., Österr. Chem. Z.*, 1925, **28**, 162

Explosive decomposition under vacuum.

See other PEROXOACID SALTS

0147. Sodium tetrahydroborate (Sodium borohydride)

[16940-66-2] **BH_4Na**



HCS 1980, 830; *RSC Lab. Hazard Data Sheet No. 39*, 1985

1. le Noble, W. J., *Chem. Eng. News*, 1983, **61**(19), 2
2. le Noble, W. J., private comm., 1983

A several year-old 100 ml glass bottle which had originally contained 25 g of the complex hydride exploded while being opened a few hours after the previous opening to remove a portion [1]. No plausible explanation can be deduced, and a dust explosion seems unlikely in view of the large initiation energy required [2].

See other GLASS INCIDENTS

Acetic acid, Dichloromethane, Methanol

Ward, D. E. *et al., Tetrahedron Lett.*, 1988, **29**, 517—520

In a general method for the selective reduction of ketones in presence of conjugated enones, this is effected by the tetrahydroborate in 1:1 methanol—dichloromethane at 75°C. In favourable cases the reaction is carried out at 20°C in dichloromethane containing a little acetic acid. It should be noted that addition of acetic acid to sodium tetrahydroborate in methanol—dichloromethane leads to vigorous evolution of much hydrogen.

See other GAS EVOLUTION INCIDENTS

Acids

Bailar, 1973, Vol. 1, 768

Interaction of sodium and other tetrahydroborates with anhydrous acids (fluorophosphoric, phosphoric or sulfuric) to generate diborane is very exothermic, and may be dangerously violent with rapid mixing. Safer methods of making diborane are detailed.

Alkali

1. Anon., *Angew. Chem. (Nachr.)*, 1960, **8**, 238
2. Volpers, —, *Proc. 1st Int. Symp. Prev. Occup. Risks Chem. Ind.*, 188—193, Heidelberg, ISSA, 1970
3. Mikheeva, V. I. *et al., Chem. Abs.*, 1969, **71**, 85064

A large volume of alkaline tetrahydroborate solution spontaneously heated and decomposed, liberating large volumes of hydrogen which burst the container. Decomposition is rapid when pH is below 10.5 [1]. A more detailed account of the investigation was published [2]. Dry mixtures with sodium hydroxide containing 15—40% of tetrahydroborate liberate hydrogen explosively at 230—270°C [3].

See other GAS EVOLUTION INCIDENTS

Aluminium chloride, Bis(2-methoxyethyl) ether

1. de Jongh, H. A. P., *Chem. Eng. News*, 1977, **55**(31), 31
2. Brown, H. C., *Chem. Eng. News*, 1977, **55**(35), 5

Addition of a 4% solution of sodium tetrahydroborate in diglyme containing 0.09% of water to a 27% solution of aluminium chloride in the same solvent led to a violent explosion, attributed to formation and ignition of hydrogen. The ignition source arose from contact of the hydroborate solution with the solid chloride, as demonstrated experimentally. Nitrogen purging is essential for all hydride reductions [1], and also for hydroboration, organoborane, Grignard and organometallic reactions generally [2]. Previous work had shown that clear solutions of the sodium tetrahydroborate—aluminium chloride reagent did not ignite in dry air, but the solid-containing reagent could lead to ignition [2].

Charcoal

Collin, P. A., Sidgwick, C., *Chemistry in Britain*, 1992, **28**(4), 324

Mixtures of charcoal and borohydride are liable to autoignition in air, the probability being higher if the charcoal has been exposed to a damp atmosphere.

See other PYROPHORIC MATERIALS

Diborane, Bis(2-methoxyethyl) ether

See Borane—tetrahydrofuran (reference 3)

Dimethylformamide

1. Yeowell, A. *et al., Chem. Eng. News*, 1979, **57**(39), 4
2. Schwartz, J. *et al., J. Org. Chem.*, 1993, **58**(18), 5005
3. Thiokol-Ventron announcement in *Cambrian News*, 1—2, May 1980, K&K Greeff Chemicals

Hot solutions of the tetrahydroborate (15.7% wt) in DMF will undergo a violent runaway thermal decomposition, the solid residue attaining a temperature of 310°C. The induction period depends on temperature, and is 45 h at 62, and 45 m at 90°C. In a plant-scale incident, an 83 kg batch led to a violent explosion, ascribed to spontaneous ignition of trimethylamine (AIT 190°C) produced by reduction of the solvent [1]. Further investigation confirmed these results, whether technical, reagent grade or redistilled dry solvent were used, the induction period being independent of added water, amine, metal salts or borate. However, addition of formic (or acetic) acid significantly reduced the induction period, and if the solvent containing 2.6% of formic acid is added to the hydride at ambient temperature, immediate and violent decomposition ensues, involving formation of sodium formyloxytrihydroborate. The latter is responsible for reduction of the amide solvent to trimethylamine. Traces of formic acid and dimethylamine are present in the commercial solvent from hydrolysis, and the latter is catalysed by water, acid or base. Hot solutions of the hydride in DMF above M concentration will soon begin to to undergo hydrolysis/reduction reactions, both of which produce formic acid and/or di- or tri-methylamine, so the decomposition is autocatalytic and soon accelerates out of control, causing gross and violent reduction of the solvent. Further investigation is reported and the greater reduction powers of the intermediate exploited [2]. Dimethylacetamide does not react violently with sodium tetrahydroborate, even at 4.7M concentration, and should be considered as a substitute solvent, particularly at higher temperatures [3].

See other GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS

Glycerol

Epshtein, N. A. *et al., Chem. Abs.*, 1987, **106**, 55145

Contact of a drop of glycerol with a flake of sodium tetrahydroborate leads to ignition, owing to thermal decomposition of the latter at above 200°. Other glycols and methanol also react exothermally, but do not ignite.

Palladium

See Palladium: Sodium tetrahydroborate

Ruthenium salts

Cusumano, J. A., *Nature*, 1974, **247**, 456

Use of borohydride solutions to reduce ruthenium salt solutions to the metal or an alloy gave solid products (possibly hydrides), which when dry, exploded violently in contact with water or when disturbed by a spatula. Hydrazine appears to be a safe reducant for ruthenium salt solutions.

Sulfuric acid

Pascal, 1961, Vol. 6, 337

Ignition may occur if the mixture is not cooled.

See other COMPLEX HYDRIDES

Trifluoroacetic acid

1. Liddle, J., *Chem. Brit.*, 2000, **36**(1) 19
2. Bretherick, L., *Chem. Brit.*, 2000, **36**(3), 20
3. Editor's speculation
4. Rohm and Haas, 2001, private communication

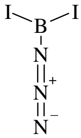
An explosion occurred during a laboratory reduction by sodium borohydride in trifluoroacetic acid. This was attributed to ignition of the hydrogen off-gas. It was resolved to use the less reactive pellets instead of borohydride powder in future[1]. Several reduction procedures add borohydride to acids. All are very inefficient and evolve much hydrogen; the actual reducant may be a borane complex. Should borane or diborane become available in the gas phase, it will create very wide explosive limits with very low ignition energies [2]. Trifluoroacetic is much more volatile than other acids used, so that small borohydride particles descending through the gas phase might react more extensively, either incandescing or generating gaseous borane, thus making hydrogen ignition more probable. It might be worth examining the stability of mixtures of hydrogen and trifluoroacetic acid vapour [3]. One borohydride manufacturer now advises against use of trifluoroacetic acid as a reduction solvent [4].

Trifluoroacetic acid

See also BORANE, FLUOROCARBONS

0148. Boron azide diiodide

[68533-38-0] **BI_2N_3**



Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 510

Decomposes explosively in contact with water.

See related NON-METAL AZIDES, NON-METAL HALIDES

0149. Boron diiodophosphide

[12228-28-3] **BI_2P**

BPI_2

Chlorine

See Chlorine: Phosphorus compounds

Metals

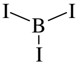
Mellor, 1947, Vol. 8, 845

It ignites in contact with mercury vapour or magnesium powder.

See related NON-METAL HALIDES

0150. Boron triiodide

[13517-10-7] **BI_3**



Though a moderately endothermic compound (ΔH_f° +70.8 kJ/mol), its high MW gives it the rather low specific energy content of 0.18 kJ/g.

Ammonia

Mellor, 1945, Vol. 5, 136

Strong exotherm on contact.

Phosphorus

Mellor, 1946, Vol. 5, 136

Warm red or white phosphorus reacts incandescently.

Water

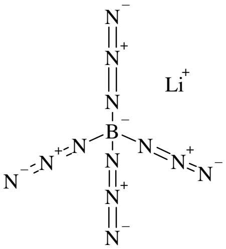
1. Moissan, H., *Compt. rend.*, 1892, **115**, 204
2. Unpublished information

Violent reaction [1], particularly with limited amounts of water [2].

See other IODINE COMPOUNDS, NON-METAL HALIDES

0151. Lithium tetraazidoborate

[ ] **$BLiN_{12}$**



Wiberg, E. *et al., Z. Naturforsch.*, 1954, **9B**, 499

Highly explosive, sensitive to heat, impact and friction (e.g. of a spatula when removing solid from a flask).

See other HIGH-NITROGEN COMPOUNDS

See related NON-METAL AZIDES

0152. Boron nitride

[10043-11-5] **BN**

$B\equiv N$

Peroxydisulfuryl difluoride

See Tetra(boron nitride) fluorosulfate

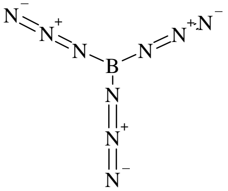
Sodium peroxide

See Sodium peroxide: Boron nitride

See related NON-METALS

0153a. Boron triazide (Triazidoborane)

[21884-15-1] **BN_9**



1. Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 27
2. Skillern, K. R. *et al., Inorg. Chem.*, 1977, **16**, 3001
3. Miller, N. E. *et al., Inorg. Chem.*, 1964, **3**, 1064

A sample of the vacuum distilled pyridine complex exploded in a heated capillary sampling tube [1]. Detonation of the trimethylamine complex [2], at or near 200°C [3] is also noted.

Diethyl ether, or Water

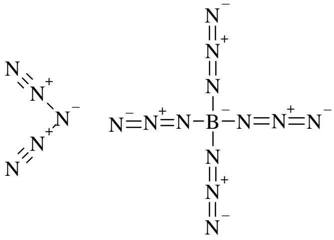
Wiberg, E. *et al., Z. Naturforsch.*, 1954, **9B**, 498

The highly explosive material detonated in contact with ether vapour or water at ambient temperature, or with ether at —35°C (probably initiated by the heat of coordination to O).

See other NON-METAL AZIDES

0153b. Pentazonium tetraazidoborate (N_5^+ tetraazidoborate)

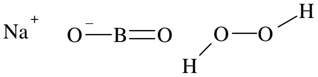
[ ] **BN_{17}**



See N_5(1+) hexaazidophosphate

0154. Sodium borate hydrogen peroxidate

[56892-92-5] [10332-33-1] **$BNaO_2.H_2O_2$**

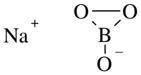


HCS 1980, 853

See Sodium peroxoborate (next below)
See entry CRYSTALLINE HYDROGEN PEROXIDATES

0155. Sodium peroxoborate

[7632-04-4] **$BNaO_3$**



1. Anon., *Angew. Chem.*, 1963, **65**, 41
2. Castrantas, 1965, 5

The true peroxoborate has been reported to detonate on light friction [1]. The common 'tetrahydrate' is not a peroxoborate, but $NaBO_2.H_2O_2.3H_2O$, and while subject to catalytic decomposition by heavy metals and their salts, or easily oxidisable foreign matter, it is relatively stable under mild grinding with other substances [2].
See also CRYSTALLINE HYDROGEN PEROXIDATES
See other CATALYTIC IMPURITY INCIDENTS, PEROXOACID SALTS

0156. Boron phosphide

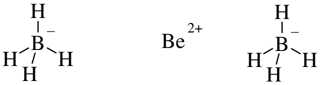
[20205-91-8] **BP**

$B{\equiv}P$

Oxidants
Sodium nitrate: Boron phosphide
See Nitric acid: Non-metals
See related NON-METALS

0157. Beryllium tetrahydroborate

[17440-85-6] **B_2BeH_8**

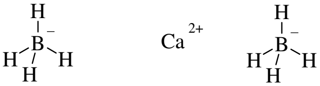


Air, or Water
1. Mackay, 1966, 169
2. Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 4

It ignites vigorously and often explodes in air [1], or on contact with cold water [2].
See other COMPLEX HYDRIDES

0158. Calcium tetrahydroborate

[17068-95-0] **B_2CaH_8**



Köster, R. *et al., Inorg. Synth.*, 1977, **17**, 18

Like other complex hydrides, it reacts vigorously with protic materials and ignition may occur.

Tetrahydrofuran

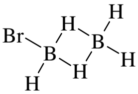
Köster, R. *et al., Inorg. Synth.*, 1977, **17**, 18

Dissolution of the 90% pure hydride in dry THF is extremely exothermic.

See other COMPLEX HYDRIDES

0159. Bromodiborane

[23834-96-0] **B_2BrH_5**



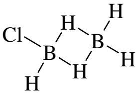
Drake, J. E., *Inorg. Synth.*, 1978, **18**, 146

May ignite violently in air.

See other HALOBORANES

0160. Chlorodiborane

[17927-57-0] **B_2ClH_5**



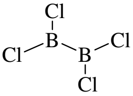
Bailar, 1973, Vol. 1, 778

A gas above —11°C, it ignites in air.

See other HALOBORANES

0161. Diboron tetrachloride

[13701-67-2] **B_2Cl_4**



Wartik, T. *et al., Inorg. Synth.*, 1967, **10**, 125

Sudden exposure to air may cause explosion.

Dimethylmercury

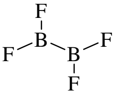
Wartik, T. *et al., Inorg. Chem.*, 1971, **10**, 650

The reaction, starting at —63°C under vacuum, exploded violently on 2 occasions after 23 uneventful runs.

See other HALOBORANES, NON-METAL HALIDES

0162. Diboron tetrafluoride

[13965-73-6] **B_2F_4**



Metal oxides

Holliday, A. K. *et al., J. Chem. Soc.*, 1964, 2732

Mixtures with mercury(II) oxide and manganese dioxide prepared at —80°C ignited at 20° and reacted violently at 15°C, respectively. Copper(II) oxide reacted vigorously at 25°C without ignition.

Oxygen

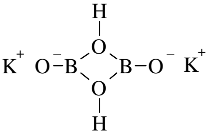
Trefonas, L. *et al., J. Chem. Phys.*, 1958, **28**, 54

The gas is extremely explosive in presence of oxygen.

See other HALOBORANES, NON-METAL HALIDES

0163. Potassium hypoborate

[63706-85-4] **$B_2H_2K_2O_4$**



Mellor, 1946, Vol. 5, 38

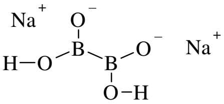
As a reducant stronger than the phosphinate, it may be expected to interact more vigorously with oxidants.

See Potassium phosphinate: Air, etc.

See other REDUCANTS

0164. Sodium hypoborate

[16903-32-5] **$B_2H_2Na_2O_4$**



Mellor, 1946, Vol. 5, 38

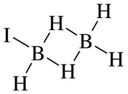
As a reducant stronger than sodium phosphinate, it may be expected to interact more vigorously with oxidants.

See Sodium phosphinate: Oxidants

See other REDUCANTS

0165. Iododiborane

[20436-27-5] **B_2H_5I**



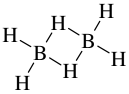
Drake, J. E., *Inorg. Synth.*, 1978, **18**, 146

May ignite violently in air.

See other HALOBORANES

†0166a. Diborane(6)

[19287-45-7] **B_2H_6**



(*MCA SD-84*, 1961); *FPA H81*, 1978; *HCS 1980*, 363 (cylinder)

Ammonia

See Diammineboronium tetrahydroborate

Benzene, or Moisture

Simons, H. P. *et al., Ind. Eng. Chem.*, 1958, **50**, 1665, 1659

Effects of presence of moisture or benzene vapour in air on the spontaneously explosive reaction have been studied.

Chlorine

See Chlorine: Non-metal hydrides

Dimethyl sulfoxide

See Dimethyl sulfoxide: Boron compounds

Halocarbons

Haz. Chem. Data, 1975, 114

Diborane reacts violently with halocarbon liquids used as vaporising fire-extinguishants.

Metals

Haz. Chem. Data, 1975, 114

Interaction with aluminium or lithium gives complex hydrides which may ignite in air.

Nitrogen trifluoride

See Nitrogen trifluoride: Diborane

Octanal oxime, Sodium hydroxide

Augustine, 1968, 78

Addition of sodium hydroxide solution during work-up of a reaction mixture of oxime and diborane in THF is very exothermic, a mild explosion being noted on one occasion.

Oxygen

Whatley, A. I. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 1997—1999

Mixtures at 105—165°C exploded spontaneously after an induction period dependent on temperature and composition.

See title reference 2

Preparative hazard

1. Mellor, 1946, Vol. 5, 36
2. Schlessinger, H. I. *et al., Chem. Rev.*, 1942, **31**, 8
3. *Hydrides of Boron and Silicon*, Stock, A. E., Ithaca, Cornell Univ. Press, 1933
4. Follet, M., *Chem. & Ind.*, 1986, 123—128
5. Hariguchi, S. *et al., Chem. Abs.*, 1989, **110**, 62931

The endothermic gas (ΔH_f° (g) +31.3 kJ/mol, 1.12 kJ/g) usually ignites in air unless dry and free of impurities [1], and ignition delays of 3—5 days, followed by violent explosions, have been experienced [2]. Explosion followed spillage of liquid diborane [3]. Problems in industrial-scale use of diborane are discussed, and the advantages of 2 new solid and non-flammable diborane complexes with 1,2-bis(*tert*-butylthio)-ethane and 1,4-bis(benzylthio)butane, and the pyrophoric complex with dimethyl sulfide are outlined [4]. Flammability limits and explosion pressures of diborane in mixtures with air, nitrogen or helium, and with hydrogen and air, have been studied. Limits for diborane—air mixtures were 0.84 to 93.3 vol%, and presence of nitrogen or helium was not effective in suppressing explosion, the limiting oxygen value being 1.3 vol%. Explosion pressure in air was 11 bar max. at 10% diborane, with a rate of rise of 1200 bar/s. Presence of hydrogen increases the explosive range. Extraordinary precautions are required for industrial use of diborane [5].

See Benzene, or Moisture, below

See Oxygen, below

See Sodium tetrahydroborate: Acids

See GAS HANDLING (reference 2)

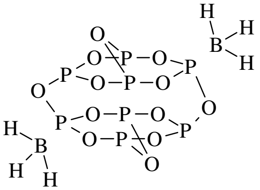
Tetravinyllead

Houben-Weyl, 1975, Vol. 13.3, 253

Interaction is explosively violent at ambient temperature.

See other BORANES, ENDOTHERMIC COMPOUNDS

0166b. Octaphosphorus dodecaoxide bis(borane)
[403499-98-9] **$B_2H_6O_{12}P_8$**

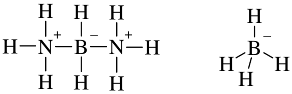


1. Tellenbach, A. *et al., Angew. Chem. (Int.)*, 2001, **40**(24), 4691
2. Tellenbach, A. *et al., Eur. J. Inorg. Chem.*, 2003, (20), 3759

An attempt to produce a phosphorus trioxide/borane complex gave this dimer on prolonged standing as an extremely explosive solid, sensitive to friction and shock even under inert gas at —30°C [1]. The X-ray structure obtained, with the two BH3 groups symmetrically associated with remote P atoms, is not easily represented in chemical bonding. Some consideration of the energetics and kinetics of the system has been given [2].

0167. Diammineboronium tetrahydroborate

[23777-63-1] **$B_2H_{12}N_2$**



1. Sidgwick, 1950, 354
2. Bailar, 1973, Vol. 1, 924

The diammine complex of diborane (formulated as above), though less reactive than diborane, ignites on heating in air [1,2].

See other COMPLEX HYDRIDES

See related BORANES

0168. Magnesium boride

[12007-25-9] **B_2Mg_3**

B^{3-} B^{3-} Mg^{2+} Mg^{2+} Mg^{2+}

Acids

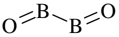
Mellor, 1946, Vol. 5, 25

The crude product containing some silicide evolves, in contact with hydrochloric or sulfuric acids, a mixture of borane and silane which may ignite.

See other METAL NON-METALLIDES

0169. Diboron oxide

[12505-77-0] **B_2O_2**



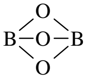
1. Merck, 1976, 1365
2. Halliday, A. K. *et al., Chem. Rev.*, 1962, **62**, 316

Probably polymeric at ambient temperature [1], at 400°C, traces of water react to cause a violent eruption and incandescence [2].

See other NON-METAL OXIDES

0170. Boron trioxide

[1303-86-2] **B_2O_3**



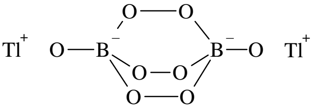
Bromine pentafluoride

See Bromine pentafluoride: Acids, etc.

See other NON-METAL OXIDES

0171. Thallium(I) peroxodiborate

[ ] **$B_2O_7Tl_2.H_2O$**



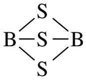
Bailar, 1973, Vol. 1, 1154

It liberates oxygen at 18°C and explodes on further warming.

See other PEROXOACID SALTS

0172. Boron trisulfide

[12007-33-9] **B_2S_3**



Chlorine

See Chlorine: Sulfides

Water

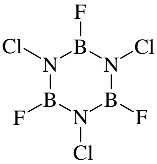
Partington, 1967, 415

Hydrolysis of the sulfide is violent.

See other NON-METAL SULFIDES

0173. 1,3,5-Trichloro-2,4,6-trifluoroborazine

[56943-26-1] **$B_3Cl_3F_3N_3$**



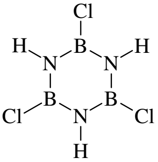
Water

Elter, G. *et al., Angew. Chem. (Intern. Ed.)*, 1975, **14**, 709

Hydrolysis of this *N*-chloro-*B*-fluoro compound is explosively violent.
See other *N*-HALOGEN COMPOUNDS, NON-METAL HALIDES

0174. *B*-1,3,5-Trichloroborazine

[26445-82-9] **$B_3Cl_3H_3N_3$**

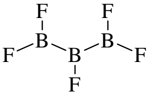


Water

Niedenzu, K. *et al., Inorg. Synth.*, 1967, **10**, 141
Hydrolysis of the *B*-chloro compound is violent.
See related NON-METAL HALIDES

0175a. Triboron pentafluoride

[15538-67-7] **B_3F_5**



Air, or Water

Timms, P. L., *J. Amer. Chem. Soc.*, 1967, **89**, 1631
It reacts explosively with air or water.

Tetrafluoroethylene

Timms, P. L., *J. Amer. Chem. Soc.*, 1967, **89**, 1631
The pentafluoride catalyses polymerisation of tetrafluoroethylene smoothly below —100°C, but explosively above that temperature.
See other NON-METAL HALIDES, POLYMERISATION INCIDENTS

0175b. 2,4,6-Triazidoborazine

[21093-86-7] **$B_3H_3N_{12}$**

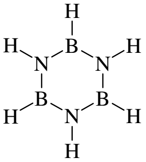
$(N_3)_3B_3H_3N_3$

1. Paine, R. T. *et al., Inorg. Chem.*, 1999, **38**(16), 3788
2. Muszkat, K. A. *et al., Isr. J. Chem.*, 1963, (1), 27

Previously reported [2] as a non-melting solid exploding on attempted purification, this proved a very shock sensitive (40 kg/cm) solid of m.p. ~150°C. Less sensitive to electrostatic discharge and friction. Methods of explosibility testing for very small quantities of very sensitive materials are described [1].
See also Borazine
See other NON-METAL AZIDES

0176. Borazine

[6569-51-3] **$B_3H_6N_3$**



Niedenzu, K. *et al., Inorg. Synth.*, 1967, **10**, 144

Samples sealed into ampoules exploded when stored in daylight, but not in the dark.

See other IRRADIATION DECOMPOSITION INCIDENTS

See related NON-METAL HYDRIDES

0177. Sodium octahydrotriborate

[12007-46-4] **B_3H_8Na**

$Na[B_3H_8]$

Solvents

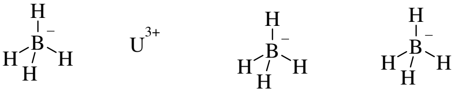
Dewkett, W. J. *et al., Inorg. Synth.*, 1974, **15**, 116

Air should not be drawn through solutions of the compound in ether, or through its solid complex with dioxane, because such materials have occasionally ignited in air.

See other COMPLEX HYDRIDES

0178. Uranium(III) tetrahydroborate

[ ] **$B_3H_{12}U$**



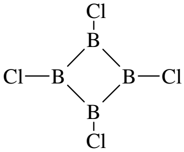
Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 4

It ignites in air and explodes on heating, unlike the U(VI) analogue.

See other COMPLEX HYDRIDES

0179. Tetraboron tetrachloride

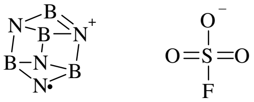
[17156-85-3] **B_4Cl_4**



Urry, G. *et al., Inorg. Chem.*, 1963, **2**, 398
Ignites in air.
See other HALOBORANES

0180. Tetra(boron nitride) fluorosulfate

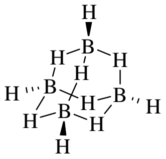
[68436-99-7] **$B_4FN_4O_3S$**



Bartlett, N. *et al., J. Chem. Soc., Chem. Comm.*, 1978, 201
Apparently thermodynamically unstable, because when the peroxodisulfuryl difluoride—boron nitride reaction mixture was heated to 40°C, detonations occurred.

0181. Tetraborane(10)

[18283-93-7] **B_4H_{10}**

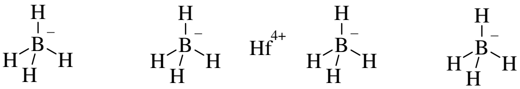


Oxidants
1. Mellor, 1946, Vol. 5, 36
2. Bailar, 1973, Vol. 1, 790

It ignites in air or oxygen, and explodes with conc. nitric acid [1]. The pure compound is stated not to ignite in air [2].
See Nitric acid: Non-metal hydrides
See other BORANES

0182. Hafnium(IV) tetrahydroborate

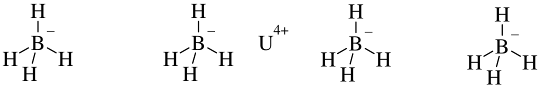
[25869-93-6] **$B_4H_{16}Hf$**



Gaylord, 1956, 58
Violent ignition on exposure to air.
See other COMPLEX HYDRIDES

0183. Uranium(IV) tetrahydroborate etherates

[65579-07-9] **$B_4H_{16}U.nR_2O$**



Water

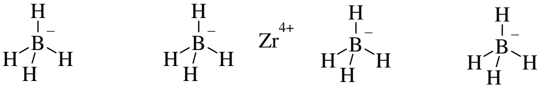
Rietz, R. R. et al., *Inorg. Chem.*, 1978, **17**, 654, 658

In contact with water, the adduct with dimethyl ether ignites and that of diethyl ether often explodes, as does invariably the bis-THF adduct.

See other COMPLEX HYDRIDES

0184. Zirconium(IV) tetrahydroborate

[23840-95-1] **$B_4H_{16}Zr$**



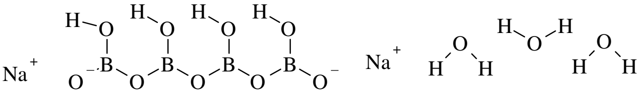
Gaylord, 1956, 58

Violent ignition on exposure to air.

See other COMPLEX HYDRIDES

0185. Sodium tetraborate

[1330-43-4] **$B_4Na_2O_7.5H_2O$**



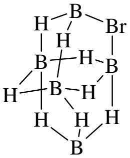
Zirconium

See Zirconium: Oxygen-containing compounds

See related METAL OXONON-METALLATES

0186. 1-Bromopentaborane(9)

[23753-67-5] **B_5BrH_8**



Air, or Hexamethylenetetramine

Remmel, R. J. *et al., Inorg. Synth.*, 1979, **19**, 248

It ignites in air and reacts explosively with hexamine above 90°C.

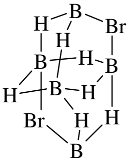
Dimethyl ether, Potassium hydride

See Potassium hydride: Bromopentaborane(9), Dimethyl ether

See other HALOBORANES

0187. 1,2-Dibromopentaborane(9)

[ ] **$B_5Br_2H_7$**



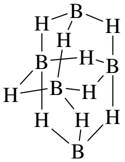
Remmel, R. J. *et al., Inorg. Synth.*, 1979, **19**, 248

It may detonate above ambient temperature.

See other HALOBORANES

†0188. Pentaborane(9)

[19624-22-7] **B_5H_9**



(*MCA SD-84*, 1961); *NSC 508*, 1979 (Boron hydrides)

McDonald, J. K. *et al., Chem. Abs.*, 2001, **135**, 65616f

The endothermic liquid ignites spontaneously in air if impure. Auto-ignition is suppressed by addition of 10% of tetrahydrofuran or dimethoxyethane. This has been made the basis of a safe hydrolytic procedure for destruction of the borane.

Ammonia

See Diammineboronium heptahydrotetraborate

Oxygen

Pentaborane, Tech. Bull. LF202, Alton (Il.), Olin Corp. Energy Div., 1960

Reaction of pentaborane with oxygen is often violently explosive.

Pentacarbonyliron, Pyrex glass

Shore, S. G. *et al., Inorg. Chem.*, 1979, **18**, 670

In the preparation of 2-(tricarbonylferra)hexaborane(10) by co-pyrolysis of the reactants in a hot-cold Pyrex tube reactor, the latter was severely etched and weakened, sometimes splintering. At 230° a maximum cumulative service life of 4 months was observed, and at 260°C the reactor was replaced at the first signs of etching, usually after 6 runs.

See other GLASS INCIDENTS

Reactive solvents

1. Cloyd, 1965, 35
2. Miller, V. R. *et al., Inorg. Synth.*, 1964, **15**, 118—122

Pentaborane is stable in inert hydrocarbon solvents but forms shock-sensitive solutions in most other solvents containing carbonyl, ether or ester functional groups and/or halogen substituents [1]. The later reference gives detailed directions for preparation and handling of this exceptionally reactive compound, including a list of 26 solvents and compounds rated as potentially dangerous in the presence of pentaborane. When large quantities are stored at low temperature in glass, a phase change involving expansion of the solid borane may rupture the container [2].

See Dimethyl sulfoxide: Boron compounds

See other GLASS INCIDENTS

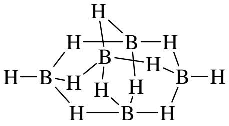
Tris(difluoroamino)fluoromethane

See Tris(difluoroamino)fluoromethane: Pentaborane(9)

See other BORANES, ENDOTHERMIC COMPOUNDS

0189. Pentaborane(11)

[18433-84-6] **B_5H_{11}**



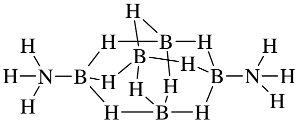
Kit and Evered, 1960, 69

Ignites in air.

See other BORANES

0190. Diammineboronium heptahydrotetraborate (Pentaborane(9) diammoniate)

[28965-70-0] **$B_5H_{15}N_2$**



Kodama, G., *J. Amer. Chem. Soc.*, 1970, **92**, 3482

The diammoniate of pentaborane(9) decomposes spectacularly on standing at ambient temperature.

See related BORANES

0191. Hexaborane(10)

[23777-80-2] **B_6H_{10}**

Complex Structure

Remmel, R. J. *et al., Inorg. Synth.*, 1979, **19**, 248

It ignites in air.

See other BORANES

0192. Hexaborane(12)
[28375-94-2] **B_6H_{12}**

See Structure

Mellor, 1946, Vol. 5, 36
It is unstable and ignites in air.
See other BORANES

0193. Lanthanum hexaboride
[12008-21-8] **B_6La**

LaB_6

See entry REFRACTORY POWDERS

0194. Caesium lithium tridecahydrononaborate
[12430-27-2] (ion) **$B_9CsH_{13}Li$**

Complex Structure

Siedle, A. R. *et al., Inorg. Chem.*, 1974, **13**, 2737
It ignites in air.
See other COMPLEX HYDRIDES

0195. Disodium tridecahydrononaborate(2—)
[119391-53-6] **$B_9H_{13}Na_2$**

Complex Structure

See Sodium tetradecahydrononaborate
See other COMPLEX HYDRIDES

0196. Sodium tetradecahydrononaborate
[70865-40-6] **$B_9H_{14}Na$**

Complex Structure

Getman, T.D. *et al, Inorg. Chem.*, 1989, **28**(8), 1507
Explosions occurred during the preparation and handling of this compound and the disodium salt.
See other COMPLEX HYDRIDES

0197. 1,10-Bis(diazonio)decaboran(8)ate
[ ] **$B_{10}H_8N_4$**

Complex Structure

The precursor is explosive.
See Ammonium decahydrodecaborate(2—): Nitrous acid
See related DIAZONIUM SALTS

0198. Decaborane(14)

[17702-41-9] **$B_{10}H_{14}$**

See Structure

Ether, or Halocarbons, or Oxygen

1. *MCA SD-84*, 1961
2. Hawthorne, M. F., *Inorg. Synth.*, 1967, **10**, 93—94
3. Shore, S. G., *Chem. Abs.*, 1986, **105**, 202122

It forms impact-sensitive mixtures with ethers (dioxane, etc.) and halocarbons (carbon tetrachloride) and ignites in oxygen at 100°C [1,2]. An improved and safer synthesis of decaborane from pentaborane is given [3].

See Dimethyl sulfoxide: Boron compounds

See other BORANES

0199. Ammonium decahydrodecaborate(2—)

[12008-61-6] **$B_{10}H_{18}N_2$**

$(NH_4)_2B_{10}H_{10}$

Nitrous acid

Knoth, W. H., *J. Amer. Chem. Soc.*, 1964, **86**, 115

Interaction of the $B_{10}H_{10}$(2—) anion with excess nitrous acid gives an inner diazonium salt (of unknown structure, possibly containing a nitronium ion) which is highly explosive in the dry state. It is readily reduced wet to the non-explosive 1,10-bis(diazonio)decaboran(8)ate inner salt.

See related BORANES

0200. Barium

[7440-39-3] **Ba**

Ba

HCS 1980, 171

Air

See Oxidising gases, below

Halocarbons

1. *Serious Accid. Ser.*, 1952, 23 and Suppl., Washington, USAEC
2. Anon., *Ind. Res.*, 1968, (9), 15
3. *Pot. Incid. Rep. 39*, ASESB, 1968
4. Stull, 1977, 25

A violent reaction occurred when cleaning lump metal under carbon tetrachloride [1]. Finely divided barium, slurried with trichlorotrifluoroethane, exploded during transfer owing to frictional initiation [2]. Granular barium in contact with fluorotrichloromethane, carbon tetrachloride, 1,1,2-trichlorotrifluoroethane, tetrachloroethylene or trichloroethylene is suceptible to detonation [3]. Thermodynamic calculations indicated a heat of decomposition of 2.60 kJ/g of mixture and a likely adiabatic temperature approaching 3000°C, accompanied by a 30-fold increase in pressure [4].

See other FRICTIONAL INITIATION INCIDENTS, METAL—HALOCARBON INCIDENTS

Interhalogens

See Bromine pentafluoride: Acids, etc.
Iodine heptafluoride: Metals

Oxidising gases

Kirk-Othmer, 1964, Vol. 3, 78

The finely divided metal may ignite or explode in air or other oxidising gases.

Water

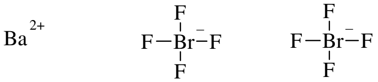
Sidgwick, 1950, 844

Interaction is more violent than with calcium or strontium, but less so than with sodium.

See other METALS, PYROPHORIC METALS

0201. Barium tetrafluorobromate

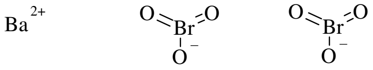
[35967-90-9] **$BaBr_2F_8$**



See entry METAL POLYHALOHALOGENATES

0202. Barium bromate

[13967-90-3] **$BaBr_2O_6$**



Hackspill, L. *et al., Compt. rend.*, 1930, **191**, 663

Thermal decomposition with evolution of oxygen is almost explosive at 300°C.

Disulfur dibromide

See Disulfur dibromide: Oxidants

Metals MRH Aluminium 6.44/22, magnesium 6.40/26

See other METAL HALOGENATES: METALS

Other reactants

Yoshida, 1980, 186

MRH values calculated for 28 combinations with oxidisable materials are given.

Sulfur MRH 2.26/12

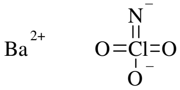
Taradoire, F., *Bull. Soc. Chim. Fr.*, 1945, **12**, 94, 447

Mixtures are unstable and may ignite 2—11 days after preparation if kept at ambient temperature, or immediately at 91—93°C. Presence of moisture (as water of crystallisation) accelerates ignition.

See other METAL HALOGENATES

0203. Barium perchlorylamide

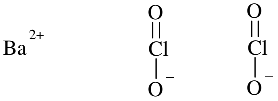
[28815-10-3] **$BaClNO_3$**



See entry PERCHLORYLAMIDE SALTS
See other *N*-METAL DERIVATIVES

0204. Barium chlorite

[14674-74-9] **$BaCl_2O_4$**

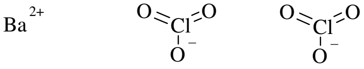


Solymosi, F. *et al., Chem. Abs.*, 1968, **68**, 51465
When heated rapidly, barium chlorite decomposes explosively at 190°C, and the lead salt at 112°C.

Dimethyl sulfate
Pascal, 1960, Vol. 16.1, 264
The sulfate ignites in contact with the unheated chlorite, presumably owing to formation of very unstable methyl chlorite.
See other CHLORITE SALTS, OXIDANTS

0205. Barium chlorate

[13477-00-4] **$BaCl_2O_6$**

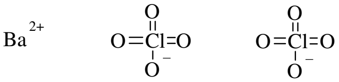


HCS 1980, 175

Other reactants
Yoshida, 1980, 72
MRH values calculated for 19 combinations with oxidisable materials are given.
See other METAL CHLORATES

0206. Barium perchlorate

[13465-95-7] **$BaCl_2O_8$**



HCS 1980, 180

Alcohols

Kirk-Othmer, 1964, Vol. 5, 75

Distillation of mixtures with C_1—C_3 alcohols gives the highly explosive alkyl perchlorates. Extreme shock-sensitivity is still shown by n-octyl perchlorate.

See ALKYL PERCHLORATES

Calcium 2,4-pentanedionate

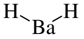
Hamid, I. *et al., Thermochim. Acta*, 1986, **101**, 189

If the ratio of the calcium chelate salt to the trihydrated barium salt in a mixture is above 2:1, the thermal decomposition during DTA/TG analysis may be explosive.

See other METAL PERCHLORATES

0207. Barium hydride

[13477-09-3] **BaH_2**



Air, or Oxygen

1. Gibson, 1969, 74
2. Mellor, 1941, Vol. 3, 650

The finely divided hydride ignites in air [1], and coarser material when heated in oxygen [2].

Metal halogenates

See METAL HALOGENATES: Metals etc.

See other METAL HYDRIDES

0208. Barium hydroxide

[17194-00-2] **BaH_2O_2**

HCS 1980, 178

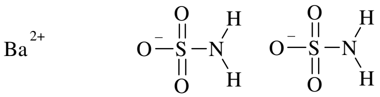
Chlorinated rubber

See CHLORINATED RUBBER: Metal oxides or hydroxides

See other INORGANIC BASES

0209. Barium amidosulfate

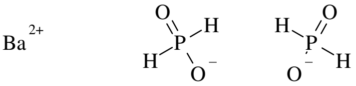
[13770-86-0] **$BaH_4N_2O_6S_2$**



Metal nitrates or nitrites

See entry METAL AMIDOSULFATES

0210. Barium phosphinate (‘Barium hypophosphite’)
[14871-79-5] **$BaH_4O_4P_2$**

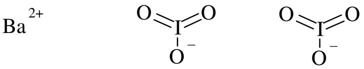


Potassium chlorate

See Potassium chlorate: Reducants

See other METAL PHOSPHINATES, REDUCANTS

0211. Barium iodate
[10567-69-8] **BaI_2O_6**



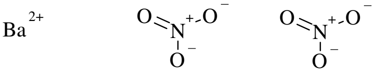
Other reactants

Yoshida, 1980, 383

MRH values calculated for 27 combinations with oxidisable materials are given.

See other METAL HALOGENATES

0212. Barium nitrate
[10022-31-8] **BaN_2O_6**



HCS 1980, 179

Aluminium, Potassium nitrate, Potassium perchlorate, Water

See Aluminium: Metal nitrates, etc.

Aluminium—magnesium alloy MRH 4.93/22 or 5.31/27

Tomlinson, W. R. *et al., J. Chem. Educ.*, 1950, **27**, 606

An intimate mixture of the finely divided components, once widely used as a photoflash composition, is readily ignitable and extremely sensitive to friction or impact.

Other reactants

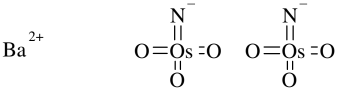
Yoshida, 1980, 202

MRH values calculated for 15 combinations with oxidisable materials are given.

See other METAL NITRATES

0213. Barium nitridoosmate

[25395-83-9] **$BaN_2O_6Os_2$**



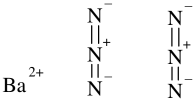
Mellor, 1942, Vol. 15, 728

Explodes at 150°C, like the ammonium salt.

See other N-METAL DERIVATIVES

0214. Barium azide

[18810-58-7] **BaN_6**



HCS 1980, 173

1. Fagan, C. P. *J. and Proc. R. Inst. Chem.*, 1947, 126
2. Ficheroulle, H. *et al., Mém. Poudres*, 1956,**33**, 7
3. Gyunter, P. L. *et al., Chem. Abs.*, 1943, **37**, 1270_9
4. Verneker, V. R-P. *et al., J. Phys. Chem.*, 1968, **72**, 778—783
5. Stull, 1977, 10

The material is impact-sensitive when dry and is supplied and stored damp with ethanol. It is used as a saturated solution and it is important to prevent total evaporation, or the slow growth of large crystals which may become dried and shock-sensitive. Lead drains must not be used, to avoid formation of the detonator, lead azide. Exposure to acid conditions may generate explosive hydrazoic acid [1]. It has been stated that barium azide is relatively insensitive to impact but highly sensitive to friction [2]. Strontium, and particularly calcium azides show much more marked explosive properties than barium azide. The explosive properties appear to be closely associated with the method of formation of the azide [3]. Factors which affect the sensitivity of the azide include surface area, solvent used and ageing. Presence of barium metal, sodium or iron ions as impurities increases the sensitivity [4]. Though not an endothermic compound (ΔH_f° —22.17 kJ/mol, 0.1 kJ/g), it may thermally decompose to barium nitride, rather than to the elements, when a considerable exotherm is produced (98.74 kJ/mol, 0.45 kJ/g of azide) [5].

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

0215. Barium oxide

[1304-28-5] **BaO**

$Ba{=}O$

Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Barium oxide

Hydroxylamine

See Hydroxylamine: Oxidants

Sulfur trioxide

See Sulfur trioxide: Metal oxides

Triuranium octaoxide

See Triuranium octaoxide: Barium oxide

Water

Bailar, 1973, Vol. 1, 638

Interaction is so vigorous and exothermic as to be a potential ignition source and fire hazard.

See other METAL OXIDES

0216. Barium peroxide

[1304-29-6] **BaO_2**

$$Ba^{2+} \quad {}^{-}O{-}O^{-}$$

HSC 1980, 181

Acetic anhydride

Rüst, 1948, 337

The peroxide was substituted for (unavailable) potassium permanganate in a process for purifying the crude anhydride in an open vessel. After several operations, when only minor explosions occurred, a violent explosion and fire occurred. Acetyl peroxide would be produced.

Calcium—silicon alloy

Smolin, A. O. *et al., Chem. Abs.*, 1976, **85**, 194906

Combustion of silico-calcium in a mixture with barium peroxide (title only translated).

Delay compositions

Stupp, J., *Chem. Abs.*, 1975, **82**, 113746

The spontaneous ignition of the peroxide in (unspecified) tracer-ignition delay compositions is described.

Hydrogen sulfide

See Hydrogen sulfide: Metal oxides

Hydroxylamine

See Hydroxylamine: Oxidants

Metals

Pascal, 1958, Vol. 4, 775

Powdered aluminium or magnesium ignite in intimate contact with the peroxide.

See also FLASH POWDER

Non-metal oxides

Pascal, 1958, Vol. 4, 773—774

The heated peroxide attains incandescence in a rapid stream of carbon dioxide or sulfur dioxide.

Organic materials, Water

Koffolt, J. H., private comm., 1966

Contact of barium peroxide and water will readily produce a temperature and a local oxygen concentration high enough to ignite many organic compounds.

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

Propane

Hoffmann, A. B. *et al., J. Chem. Educ.*, 1974, **51**, 419 (footnote 7)

Heating barium peroxide under gaseous propane at ambient pressure caused a violent exothermic reaction which deformed the glass container.

See other GLASS INCIDENTS

Selenium

Johnson, L. B., *Ind. Eng. Chem.*, 1960, **52**, 241—244

Powdered mixtures ignite at 265°C.

Wood

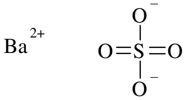
1. Dupré, A., *J. Soc. Chem. Ind.*, 1897, **16**, 492
2. Anon., *Jahresber.*, 1987, 66

Friction of the peroxide between wooden surfaces ignited the latter [1]. A granulated and dried priming composition, largely consisting of barium peroxide, was being sieved by hand to break up agglomerated lumps. Towards the end of the operation, ignition occurred. This was caused by rubbing contact of the priming mixture with the sloping plywood frame of the sieve as the composition was pressed through [2].

See other FRICTIONAL INITIATION INCIDENTS, METAL PEROXIDES, OXIDANTS

0217. Barium sulfate

[7727-43-7] **BaO_4S**



Aluminium

See Aluminium: Metal oxides, or Oxosalts

Phosphorus

See Phosphorus: Metal sulfates

See other METAL OXONON-METALLATES

0218. Barium sulfide

[21109-95-5] **BaS**

$Ba{=}S$

HCS 1980, 182

Dichlorine oxide

See Dichlorine oxide: Oxidisable materials

Oxidants

Mellor, 1941, Vol. 3, 745

Barium sulfide explodes weakly on heating with lead dioxide or potassium chlorate, and strongly with potassium nitrate. Calcium and strontium sulfides are similar.

Phosphorus(V) oxide

Pascal, 1958, Vol. 4, 832

Interaction is violent, attaining incandescence.

See other METAL SULFIDES

0219. Barium nitride

[12047-79-9] **Ba_3N_2**

$Ba^{2+} \quad Ba^{2+} \quad Ba^{2+} \quad N^{3-} \quad N^{3-}$

Air, or Water

Sorbe, 1968, 34

It reacts violently with air or water.

See Barium azide (reference 5)

See other *N*-METAL DERIVATIVES

0220. Beryllium

[7440-41-7] **Be**

Be

HCS 1980, 207; *RSC Lab. Hazards Data Sheet No. 67*, 1988 (Be and compounds)

Carbon dioxide, Nitrogen

See Carbon dioxide: Metals, Nitrogen

Halocarbons

Pot. Incid. Rep. 39, ASESB, 1968

Mixtures of powdered beryllium with carbon tetrachloride or trichloroethylene will flash on heavy impact.

See other METAL—HALOCARBON INCIDENTS

Halogens

Pascal, 1958, Vol. 4, 22

Warm beryllium incandesces in fluorine or chlorine.

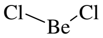
Phosphorus

See Phosphorus: Metals

See other METALS

0221. Beryllium chloride

[7787-47-5] **$BeCl_2$**



Sulfur nitrides

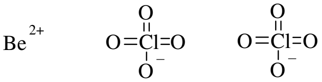
See Disulfur dinitride: Metal chlorides

Tetrasulfur tetranitride: Metal chlorides

See other METAL HALIDES

0222. Beryllium perchlorate

[13597-95-0] **$BeCl_2O_8$**



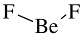
Laran, R. J., US Pat. 3 157 464, 1964

A powerful oxidant, insensitive to heat or shock and useful in propellant and igniter systems.

See other METAL PERCHLORATES

0223. Beryllium fluoride

[7787-49-7] **BeF_2**



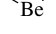
Magnesium

See Magnesium: Beryllium fluoride

See other METAL HALIDES

0224. Beryllium hydride

[7787-52-2] **BeH_2**



Methanol, or Water

1. Barbaras, G. D., *J. Amer. Chem. Soc.*, 1951, **73**, 48
2. Brendel, G. J. *et al., Inorg. Chem.*, 1978, **17**, 3589

Reaction of the ether-containing hydride with methanol or water is violent, even at —196°C [1]. A crystalline modification produced by pressure-compaction of the hydride reacts slowly with moist air or water [2].

See other METAL HYDRIDES

0225. Beryllium oxide

[1304-56-9] **BeO**

$Be{=}O$

HCS 1980, 208

Magnesium

See Magnesium: Metal oxides

See other METAL OXIDES

0226. Bismuth

[7440-69-9] **Bi**

Bi

Aluminium

See Aluminium: Bismuth

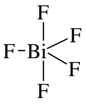
Oxidants

See Ammonium nitrate: Metals
Bromine pentafluoride: Acids, etc.
Chloric acid: Metals, etc.
Iodine pentafluoride: Metals
Nitric acid: Metals
Nitrosyl fluoride: Metals
Perchloric acid: Bismuth

See other METALS

0227. Bismuth pentafluoride

[7787-62-4] **BiF_5**



Water

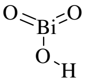
von Wartenberg, H., *Z. Anorg. Chem.*, 1940, **224**, 344

It reacts vigorously with water, sometimes igniting.

See other METAL HALIDES

0228. Bismuthic acid (Bismuth oxide hydroxide)

[22750-47-6] **$BiHO_3$**



Hydrofluoric acid

Mellor, 1939, Vol. 9, 657

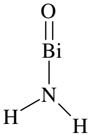
Interaction of the solid acid with 40% hydrofluoric acid is violent, ozonised oxygen being evolved.

See other OXIDANTS

See related INORGANIC ACIDS

0229. Bismuth amide oxide

[ ] **BiH_2NO**



Watt, G. W. *et al., J. Amer. Chem. Soc.*, 1939, **61**, 1693

The solid, prepared in liquid ammonia, explodes when free of ammonia and exposed to air.

See other *N*-METAL DERIVATIVES

0230. Bismuth nitride

[12232-97-2] **BiN**

$Bi \equiv N$

Alone, or Water

1. Fischer, F. *et al., Ber.*, 1910, **43**, 1471
2. Franklin, E. C., *J. Amer. Chem. Soc.*, 1905, **27**, 847

Very unstable, exploded on shaking [1] or heating, or in contact with water or dilute acids [2].

See other *N*-METAL DERIVATIVES, METAL NON-METALLIDES

0231. Plutonium bismuthide

[12010-53-6] **BiPu**

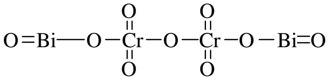
Pu^{3+} Bi^{3-}

Williamson, G. K., *Chem. & Ind.*, 1960, 1384

Extremely pyrophoric.

See other ALLOYS, PYROPHORIC MATERIALS

0232. Dibismuth dichromium nonaoxide (‘Bismuth chromate’)
[37235-82-8] **$Bi_2Cr_2O_9$**



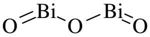
Hydrogen sulfide

Pascal, 1960, Vol. 13.1, 1025

The gas may ignite on contact with the ‘chromate’.

See other METAL OXIDES, METAL OXOMETALLATES

0233. Bismuth trioxide
[1304-76-3] **Bi_2O_3**



Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Potassium

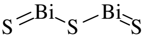
See Potassium: Metal oxides

Sodium

See Sodium: Metal oxides

See other METAL OXIDES

0234. Bismuth trisulfide
[1345-07-9] **Bi_2S_3**



Preparative hazard

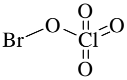
Glatz, A. C. *et al., J. Electrochem. Soc.*, 1963, **110**, 1231

Possible causes of explosions in direct synthesis are discussed.

See Sulfur: Metals

See other METAL SULFIDES

0235. Bromine perchlorate
[32707-10-1] **$BrClO_4$**



Schack, C. J. *et al., Inorg. Chem.*, 1971, **10**, 1078

It is shock-sensitive.

Perfluorobutadiene

Schack. C. J. *et al., Inorg. Chem.*, 1975, **14**, 151 (footnote 8)

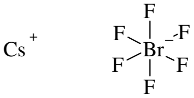
During adduct formation, the perchlorate must be present in excess to prevent formation of a mono-adduct, which may well be explosive.

See Chlorine perchlorate: Chlorotrifluoroethylene

See other GLASS INCIDENTS, HALOGEN OXIDES

0236. Caesium hexafluorobromate

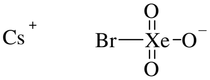
[26222-92-4] **$BrCsF_6$**



See entry METAL POLYHALOHALOGENATES

0237. Caesium bromoxenate

[ ] **$BrCsO_3Xe$**



Water

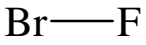
Jaselskis, B. *et al., J. Amer. Chem. Soc.*, 1969, **91**, 1875

Aqueous solutions are extremely unstable and caution is required if isolation of the compound is contemplated.

See other XENON COMPOUNDS

0238. Bromine fluoride

[13863-59-7] **BrF**



Sidgwick, 1950, 1149

Chemically it behaves like the other bromine fluorides, but is more reactive.

Hydrogen

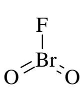
Pascal, 1960, Vol. 16.1, 412

Hydrogen ignites in the fluoride at ambient temperature.

See other INTERHALOGENS

0239. Bromyl fluoride

[22585-64-4] **$BrFO_2$**



Water

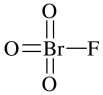
Bailar, 1973, Vol. 2, 1388

Hydrolysis may proceed explosively.

See other HALOGEN OXIDES

0240. Perbromyl fluoride

[25251-03-0] **$BrFO_3$**



Fluoropolymers

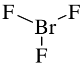
Johnson, K. G. *et al., Inorg. Chem.*, 1972, **11**, 800

It is considerably more reactive than perchloryl fluoride, and attacks glass and the usually inert polytetrafluoroethylene and polychlorotrifluoroethylene.

See other CORROSION INCIDENTS, GLASS INCIDENTS, HALOGEN OXIDES

0241. Bromine trifluoride

[7787-71-5] **BrF_3**



1. Davis, R. A. *et al., J. Org. Chem.*, 1962, **32**, 3478
2. Musgrave, W. K. R., *Advan. Fluorine Chem.*, 1964, **1**, 12

The hazards and precautions in use of this very reactive fluorinating agent are outlined [1]. Contact with rubber, plastics or other organic materials may be explosively violent and reaction with moisture is very vigorous [2].

Ammonium halides

Sharpe, A. G. *et al., J. Chem. Soc.*, 1948, 2137

Explosive reaction.

Antimony(III) chloride oxide

Mellor, 1956, Vol. 2, Suppl. 1, 166

Interaction is violent, even more so than with antimony trioxide.

Carbon monoxide

Mellor, 1956, Vol. 2, Suppl. 1, 166

At temperatures rather above 30°C, explosions occurred.

Carbon tetrachloride

Dixon, K. R. *et al., Inorg. Synth.*, 1970, **12**, 233

Excess bromine trifluoride may be destroyed conveniently in a hood by slow addition to a large volume of the solvent, interaction being vigorous but not dangerous.

See Solvents, below

Halogens, or Metals, or Non-metals, or Organic materials

1. Mellor, 1941, Vol. 2, 113; 1956, Vol. 2, Suppl. 1, 164—167
2. 'Chlorine Trifluoride Tech. Bull.', Morristown, Baker & Adamson, 1970

Incandescence is caused by contact with bromine, iodine, arsenic, antimony (even at —10°C); powdered molybdenum, niobium, tantalum, titanium, vanadium; boron, carbon, phosphorus or sulfur [1]. Carbon tetraiodide, chloromethane, benzene or ether ignite or explode on contact, as do organic materials generally. Silicon also ignites [2].

See Uranium, below

2-Pentanone

Stevens, T. E., *J. Org. Chem.*, 1961, **26**, 1629 (footnote 11)

During evaporation of solvent hydrogen fluoride, an exothermic reaction between residual ketone and bromine trifluoride set in and accelerated to explosion.

Potassium hexachloroplatinate

Dixon, K. R. *et al., Inorg. Synth.*, 1970, **12**, 233—237

Interaction of the reagents in bromine as diluent to produce the trichlorotrifluoro- and then hexafluoro-platinates is so vigorous that increase in scale above 1g of salt is not recommended.

Pyridine

Kirk-Othmer, 1966, Vol. 9, 592

The solid produced by action of bromine trifluoride on pyridine in carbon tetrachloride ignites when dry. 2-Fluoropyridine reacts similarly.

Silicone grease

Sharpe, A. G. *et al., J. Chem. Soc.*, 1948, 2136

As it reacts explosively in bulk, the amount of silicone grease used on joints must be minimal.

Solvents

1. Sharpe, A. G. *et al., J. Chem. Soc.*, 1948, 2135
2. Simons, J. H., *Inorg. Synth.*, 1950, **3**, 185

Bromine trifluoride explodes on contact with acetone or ether [1], and the frozen solid at —80°C reacts violently with toluene at that temperature [2].

See Halogens, etc., above

Tin(II) chloride

Mellor, 1956, Vol. 2, Suppl. 1, 165

Contact causes ignition.

Uranium, Uranium hexafluoride

Johnson, K. *et al., 6th Nucl. Eng. Sci. Conf.*, New York, 1960. Reprint Paper No. 23

Uranium may ignite or explode during dissolution in bromine trifluoride, particularly when high concentrations of the hexafluoride are present. Causative factors are identified.

See Halogens, etc. above

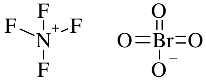
Water

1. Mellor, 1941, Vol. 2, 113
2. *491M*, 1975, 73

Interaction is violent, oxygen being evolved [1], and even at —50°C, reaction with 6N hydrochloric acid is explosive [2].

See other INTERHALOGENS

0242. Tetrafluoroammonium perbromate
[25483-10-7] **BrF_4NO_4**

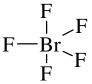


Christe, K. O. *et al., Inorg. Chem.*, 1980, **19**, 1495

Solutions in hydrogen fluoride at —78°C exploded when isolation of the salt was attempted.

See other *N*-HALOGEN COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

0243. Bromine pentafluoride
[7789-30-2] **BrF_5**



Acetonitrile

1. Meinert, H. *et al., Z. Chem.*, 1969, **9**, 190
2. Stein, L., *Chem. Eng. News*, 1984, **62**(28), 4

Although solutions of bromine pentafluoride in acetonitrile were reported stable at ambient temperature [1], it has been found that a 9% solution in the anhydrous solvent prepared at —196°C decomposed violently, bursting the container, about 1 h after attaining ambient temperature [2].

See Hydrogen-containing materials, below

Acids, or Halogens, or Metal halides, or Metals, or Non-metals, or Oxides

1. Mellor, 1956, Vol. 2, Suppl. 1, 172
2. Sidgwick, 1950, 1158

Contact with the following at ambient or slightly elevated temperatures is violent, ignition often occurring: strong nitric acid or sulfuric acids; chlorine (explodes on heating), iodine; ammonium chloride, potassium iodide; antimony, arsenic, boron powder, selenium, tellurium; aluminium powder, barium, bismuth, cobalt powder, chromium, iridium powder, iron powder, lithium powder, manganese, molybdenum, nickel powder, rhodium powder, tungsten, zinc; charcoal, red phosphorus, sulfur, arsenic pentoxide, boron trioxide, calcium oxide, carbon monoxide, chromium trioxide, iodine pentoxide, magnesium oxide, molybdenum trioxide, phosphorus pentoxide, sulfur dioxide or tungsten trioxide [1,2].

Hydrogen-containing materials

1. Mellor, 1956, Vol. 2, Suppl. 1, 172
2. Braker, 1980, 56

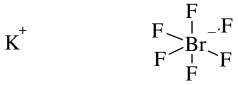
Contact with the following materials, containing combined hydrogen, is likely to cause fire or explosion: acetic acid, ammonia, benzene, ethanol, hydrogen, hydrogen sulfide, methane; cork, grease, paper, wax, etc. The carbon content further contributes to the observed reactivity [1]. Chloromethane reacts with explosive violence [2].
See Acetonitrile, above

Perchloryl perchlorate
See Perchloryl perchlorate: Bromine pentafluoride

Water
Sidgwick, 1950, 1158
Contact with water causes a violent reaction or explosion, oxygen being evolved.
See other INTERHALOGENS

0244. Potassium hexafluorobromate

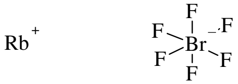
[32312-22-4] **BrF_6K**



See entry METAL POLYHALOHALOGENATES

0245. Rubidium hexafluorobromate

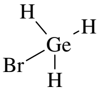
[32312-23-5] **BrF_6Rb**



See entry METAL POLYHALOHALOGENATES

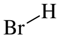
0246. Bromogermane

[13569-43-2] **$BrGeH_3$**



Preparative hazard
See Bromine: Germane
See related METAL HYDRIDES

0247. Hydrogen bromide
[10035-10-6] **BrH**



HCS 1980, 545 (cylinder gas), 538 (48% solution)

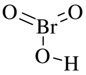
Ammine-1,2-diaminoethanediperoxochromium(IV)
See Ammine-1,2-diaminoethanediperoxochromium(IV): Hydrogen bromide

Fluorine
See Fluorine: Hydrogen halides

Ozone
See Ozone: Hydrogen bromide
See other INORGANIC ACIDS, NON-METAL HALIDES, NON-METAL HYDRIDES

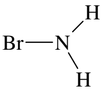
Preparative hazard
See Bromine: Phosphorus

0248. Bromic acid
[7789-31-3] **$BrHO_3$**



In contact with oxidisable materials, reactions are similar to those of the metal bromates.
See entry METAL HALOGENATES
See other INORGANIC ACIDS, OXOHALOGEN ACIDS

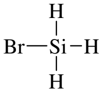
0249. Bromamine (Bromamide)
[14519-10-9] **BrH_2N**



Jander, J. *et al., Z. Anorg. Chem.*, 1958, **296**, 117
The isolated material decomposes violently at —70°C, while an ethereal solution is stable for a few hours at that temperature.
See other *N*-HALOGEN COMPOUNDS

†0250. Bromosilane

[13465-73-1] **BrH_3Si**



Ward, L. G. L., *Inorg. Synth.*, 1968, **11**, 161
Ignites in air (gas above 2°C).
See other HALOSILANES

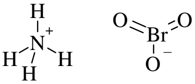
0251. Ammonium bromide

[12124-97-9] **BrH_4N**

Bromine trifluoride
See Bromine trifluoride: Ammonium halides
See related METAL HALIDES

0252. Ammonium bromate

[13483-59-5] **BrH_4NO_3**



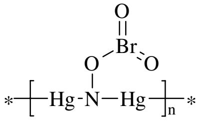
1. Sorbe, 1968, 129
2. Shidlovskii, A. A. *et al., Chem. Abs.*, 1968, **69**, 78870

It is a combustible and explosive salt which is very friction-sensitive [1], and may explode spontaneously [2].

Other reactants
Yoshida, 1980, 180
MRH values calculated for 16 combinations with oxidisable materials are given.
See other OXOSALTS OF NITROGENOUS BASES

0253. Poly(dimercuryimmonium bromate)

[ ] **$(BrHg_2NO_3)_n$**



Sorbe, 1967, 97
Highly explosive.
See entry POLY(DIMERCURYIMMONIUM) COMPOUNDS

0254. Iodine bromide

[7789-33-5] **BrI**

I—Br

Metals

1. Mellor, 1961, Vol. 2, Suppl. 2, 452; 1963, Suppl. 3, 1563
2. Pascal, 1963, Vol. 8.3, 308

A mixture with sodium explodes under a hammer blow, while potassium explodes strongly under the molten bromide [1]. Tin reacts violently with the bromide [2].

Phosphorus

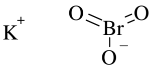
Mellor, 1963, Vol. 2, Suppl. 3, 264

Phosphorus reacts violently with the molten bromide.

See other INTERHALOGENS, IODINE COMPOUNDS

0255. Potassium bromate

[7758-01-2] **$BrKO_3$**



$K^+ \quad BrO_3^-$

HCS 1980, 760

Anon., Personal communication, 1999

A factory using potassium bromate regularly in small portions found that it caked in storage and had to be broken up. A largely full, but year old, polythene lined fibreboard drum thereof was broken by stabbing the contents with a, possibly rusty, knife and the lumps needed for use removed by gloved hand. The 1.5 kg so removed was observed to be fizzing and was sprayed with water. Minutes later, the 18 kg remaining in the drum deflagrated brightly, described as “sunrise behind the reactor”, and ignited a sack of monomer nearby. Water extinguished the fire in a few minutes. Although bromates are thermodynamically unstable with respect to bromides, and there may have been slight surface contamination with organics, propagation of a surface reaction is hard to explain. The packaging would be a substantial fuel, but mixing with that is very poor. The exact cause remains mysterious. The business has decided to buy bromate in smaller lots and to subdivide those into individual 1.5 kg charges when received and before caking can occur. The operators have decided to no longer break up caked chemicals by jumping on the polythene liners containing them.

Aluminium, Dinitrotoluene

Yoshinaga, S. *et al., Chem. Abs.*, 1980, **92**, 44080

The mixture reacts violently at 290°C, with enormous gas evolution and is used to fracture concrete. The mechanism was studied.

See other GAS EVOLUTION INCIDENTS

Azoformamide

Vidal, F. D. *et al., Bakers Dig.*, 1979, **53**(3), 16—18

A mixture of the oxidant and blowing agent (2:1) is used as a dough improver. Potential problems of incompatibility during tableting operations were overcome by incorporating hydrated salts into the tableting formulation.

Ceric ammonium nitrate, Malonic acid, Water

Bartmess, J. *et al., Chem. Eng. News*, 1998, **76**(24), 4

Subsequent to a fire in a teaching laboratory, it was discovered that a mixture of equal weights of the three dry solids, itself stable, reacted violently when wetted with up to two parts of water and was capable of igniting paper. All components (which exhibit an oscillating chemical reaction in solution) were necessary for this effect.

Disulfur dibromide

See Disulfur dibromide: Oxidants

Non-metals MRH Sulfur 2.55/14

1. Taradoire, F., *Bull. Soc. Chim. Fr.*, 1945, **12**, 94, 466
2. Pascal, 1961, Vol. 6, 440

Mixtures with sulfur are unstable, and may ignite some hours after preparation, depending on the state of subdivision and atmospheric humidity [1]. Selenium reacts violently with aqueous solutions of the oxidant [2].

Other reactants

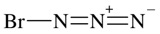
Yoshida, 1980, 181—182

MRH values calculated for 28 combinations with oxidisable materials are given.

See other METAL OXOHALOGENATES, OXIDANTS

0256. Bromine azide

[13973-87-0] **BrN_3**



$Br{-}N{=}\overset{+}{N}{=}N^{-}$

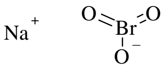
1. Hargittai, M. *et al., Angew. Chem. (Int.)*, 1993, **32**, 759
2. Mellor, 1940, Vol. 8, 336
3. Tornieporth-Oetting, I. C. *et al., Angewand. Chem. (Int.)*, 1995, **34**(5), 511

The solid, liquid and vapour are all very shock-sensitive [1]. The liquid explodes on contact with arsenic; sodium, silver foil; or phosphorus. Explosion is likely to be triggered by pressure fluctuations of around 10 Pa [3]. Concentrated solutions in organic solvents may explode on shaking [2].

See other ENDOTHERMIC COMPOUNDS, HALOGEN AZIDES

0257. Sodium bromate

[7789-38-0] **$BrNaO_3$**



HCS 1970, 831

Fluorine

See Fluorine: Sodium bromate

Grease

1. *MCA Case History No. 874*
2. Stull, 1977, 28—29

A bearing assembly from a sodium bromate crusher had been degreased at 120°C, and while still hot the sleeve was hammered to free it. The assembly exploded violently, probably because of the presence of a hot mixture of sodium bromate and a grease component (possibly a sulfurised derivative). It is known that mixtures of bromates and organic or sulfurous matter are heat- and friction-sensitive [1]. The energy of decomposition of the likely components has been calculated as 1.93 kJ/g, with an explosion temperature above 2000°C [2].

Other reactants

Yoshida, 1980, 184—185

MRH values calculated for 29 combinations with oxidisable materials are given.

See other METAL OXOHALOGENATES

0258. Bromine dioxide

[21255-83-4] **BrO_2**

$O{=}Br{=}O$

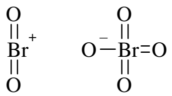
Brauer, 1963, Vol. 1, 306

Unstable unless stored at low temperatures, it may explode if heated rapidly.

See other HALOGEN OXIDES

0259. Bromine trioxide

[32062-14-9] **BrO_3**



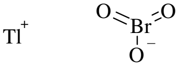
$O{=}Br^{+}{=}O \qquad {}^{-}O{-}Br({=}O)_2{=}O$

1. Lewis, B. *et al., Z. Elektrochem.*, 1929, **35**, 648—652
2. Pflugmacher, A. *et al., Z. Anorg. Chem.*, 1955, **279**, 313

The solid produced at —5°C by interaction of bromine and ozone is only stable at —80°C or in presence of ozone, and decomposition may be violently explosive in presence of trace impurities [1]. The structure may be the dimeric bromyl perbromate, analogous to Cl_2O_6 [2].

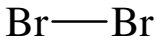
See other CATALYTIC IMPURITY INCIDENTS, HALOGEN OXIDES

0260. Thallium bromate
[14550-84-6] BrO$_3$Tl



Pascal, 1961, Vol. 6, 950
It decomposes explosively around 140°C.
See other HEAVY METAL DERIVATIVES, METAL OXOHALOGENATES

0261. Bromine
[7726-95-6] Br$_2$



(*MCA SD-49*, 1968); *NSC 313*, 1979; *FPA H61*, 1977; *HCS 1980*, 218
RSC Lab. Hazard Data Sheet No. 24, 1984

Berthelot, J. *et al., J. Chem. Educ.*, 1986, **63**(11), 1011
The stable complex of bromine with tetrabutylammonium bromide is safer and more easily handled than bromine itself.

Acetone MRH 0.46/16
Levene, P. A., *Org. Synth.*, 1943, Coll. Vol. 2, 89
During bromination of acetone to bromoacetone, presence of a large excess of bromine must be avoided to prevent sudden and violent reaction.
See Carbonyl compounds, below

Acetonitrile, Ethyl 2-methoximino-3-oxobutanoate
Personal experience
An attempt to brominate the butanoate as a concentrated solution in acetonitrile showed reversible discoloration of bromine on cooling. At around 5°C near-white needles crystallised, after filtration and allowing to warm to room temperature these decomposed exothermically with vigorous fume evolution. Tlc suggested they did not contain the butanoate, or its bromination products.

Acetylene MRH 8.70/100
See Acetylene: Halogens

Acrylonitrile MRH 2.84/100
See Acrylonitrile: Halogens

Alcohols
1. Muir, G. D., *Chem. Brit.*, 1972, **8**, 16
2. Bush, E. L., private comm., 1968
3. Desty, D. H., private comm., 1986

Reaction with methanol may be vigorously exothermic. A mixture of bromine (9 ml) and methanol (15 ml) boiled in 2 m and in a previous incident such a mixture had erupted from a measuring cylinder [1]. The exotherm with industrial methylated

spirits (ethanol containing 5% methanol) is much greater, and addition of 10 ml of bromine to 40 ml of IMS rapidly causes violent boiling [2]. A further case of ejection of a methanol solution of bromine from a measuring cylinder was described [3].
See other HALOGENATION INCIDENTS

Aluminium, Dichloromethane
Nolan, 1983, Case History 26
Bromochloromethane was being prepared in a 400 l reactor by addition of liquid bromine to dichloromethane in presence of aluminium powder (which would form some aluminium bromide to catalyse the halogen exchange reaction). The reaction was started and run for 1.5 h, stopped for 8 h, then restarted with addition of bromine at double the usual rate for 2.5 h, though the reaction did not appear to be proceeding. Soon afterwards a thermal runaway occurred, shattering the glass components of the reactor.
See other GLASS INCIDENTS, HALOGENATION INCIDENTS

Ammonia
Mellor, 1967, Vol. 8, Suppl. 2, 417
Interaction at normal or elevated temperatures, followed by cooling to —95°C, gives an explosive red oil.
See Nitrogen tribromide hexaammoniate

Boron
See Boron: Halogens
See Phosphorus: Halogens

3-Bromopropyne
See 3-Bromopropyne, (reference 3)
See Chlorine: 3-Chloropropyne

Carbonyl compounds
MCA SD-49, 1968
Organic compounds containing active hydrogen atoms adjacent to a carbonyl group (aldehydes, ketones, carboxylic acids) may react violently in unmoderated contact with bromine.
See Acetone, above

Chlorotrifluoroethylene, Oxygen
Haszeldine, R. N. *et al., J. Chem. Soc.*, 1959, 1085
Addition of bromine to the gas-phase mixture initiated an explosion, but see Oxygen: Halocarbons (reference 3).

Copper(I) hydride
See Copper(I) hydride: Halogens

Diethyl ether
1. Tucker, H., private comm., 1972
2. Anon., *Safety Digest Univ. Safety Assoc.*, 1989, **34**, 14

Shortly after adding bromine to ether the solution erupted violently (or exploded softly). Photocatalytic bromination may have been involved [1]. Spontaneous ignition occurred on addition of ether to impure bromine [2].
See Tetrahydrofuran, below; or Chlorine: Diethyl ether

Diethylzinc
Houben-Weyl, 1973, Vol. 13.2a, 757
Interaction without diluents may produce dangerous explosions. Even with diluents (ether), interaction of dialkylzincs with halogens is initially violent at 0 to —20°C.

Dimethylformamide
Tayim, H. A. *et al., Chem. & Ind.*, 1973, 347
Interaction is extremely exothermic, and under confinement in an autoclave the internal temperature and pressure exceeded 100°C and 135 bar, causing failure of the bursting disc. The product of interaction is dimethylhydroxymethylenimmonium bromide, and the explosive decomposition may have involved formation of *N*-bromodimethylamine, carbon monoxide and hydrogen bromide.
See *N*-HALOGEN COMPOUNDS

Ethanol, Phosphorus
Read, C. W. W., *School Sci. Rev.*, 1940, **21**(83), 967
The vigorous interaction of ethanol, phosphorus and bromine to give bromoethane is considered too dangerous for a school experiment.

Fluorine
See Fluorine: Halogens

Germane
Swiniarski, M. F. *et al., Inorg. Synth.*, 1974, **15**, 157—160
During the preparation of mono- or di-bromogermane, either the scale of operation or the rate of addition of bromine must be closely controlled to prevent explosive reaction occurring.
See Non-metal hydrides, below

Hydrogen
Mellor, 1956, Vol. 2, Suppl. 1, 707
Combination is explosive under appropriate temperature and pressure conditions.

Isobutyrophenone
MCA Guide, 1972, 307
Bromine was added dropwise at 20—31°C to a solution of the ketone in carbon tetrachloride. The completed reaction mixture was cooled in ice, but exploded after 15 m.
See other HALOGENATION INCIDENTS

Metal acetylides and carbides
Several of the mono- and di-alkali metal acetylides and copper acetylides ignite at ambient temperature or on slight warming, with either liquid or vapour. The alkaline earth, iron, uranium and zirconium carbides ignite in the vapour on heating.
See Calcium acetylide: Halogens

Caesium acetylide: Halogens
Dicopper(I) acetylide: Halogens
Iron carbide: Halogens
Lithium acetylide: Halogens
Rubidium acetylide: Halogens
Strontium acetylide: Halogens
Uranium dicarbide: Halogens
Zirconium dicarbide: Halogens

Metal azides

Mellor, 1940, Vol. 8, 336

Nitrogen-diluted bromine vapour passed over silver azide or sodium azide formed bromine azide, and often caused explosions.

Metals MRH Aluminium 1.96/10

1. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
2. Mellor, 1941, Vol. 2, 469; 1963, Vol. 2, Suppl. 2.2, 1563, 2174
3. *MCA SD-49*, 1968
4. Mellor, 1941, Vol. 7, 260
5. Mellor, 1939, Vol. 3, 379
6. Hartgen, C. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 70

Lithium is stable in contact with dry bromine, but heavy impact will initiate explosion, while sodium in contact with bromine needs only moderate impact for initiation [1]. Potassium ignites in bromine vapour and explodes violently in contact with liquid bromine, and rubidium ignites in bromine vapour [2]. Aluminium, mercury or titanium react violently with dry bromine [3]. Warm germanium ignites in bromine vapour [4], and antimony ignites in bromine vapour and reacts explosively with the liquid halogen [5]. During preparation of praseodymium bromide, accidental contact of liquid bromine with small particles of praseodymium led to a violent explosion [6].

See Gallium: Halogens

Nitromethane

Rochat, A. C., private comm., 1990.

A solution of bromine (116 g) in nitromethane (300 ml) was employed in an attempt to brominate a pigment (30 g). On heating the mix in an autoclave, runaway commenced at 70°C, soon shattering the vessel. Nitromethane being an explosive of low oxygen balance, the potential energy certainly, and the sensitivity probably, will be increased by bromine or bromination. Bromonitromethane salts and formaldehyde adducts thereof are intermediates in manufacture of some disinfectants; isolation of the first is considered most unsafe in the industry, the second are thought to need careful handling.

See Nitromethane, Chloronitromethane.

Non-metal hydrides

1. Stock, A. *et al., Ber.*, 1917, **50**, 1739
2. Sujishi, S. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 4631
3. Geisler, T. C. *et al., Inorg. Chem.*, 1972, **11**, 1710
4. Merck, 1976, 955

Interaction of silane and its homologues with bromine at ambient temperature is explosively violent [1] and temperatures of below —30°C are necessary to avoid ignition of the reactants [2]. Ignition of disilane at —95°C and of germane at —112°C emphasises the need for good mixing to dissipate the large exotherm [3]. Phosphine reacts violently with bromine at ambient temperature [4].
See Ethylphosphine: Halogens, or Phosphine: Halogens

Other reactants
Yoshida, 1980, 179
MRH values for 10 combinations with reactive materials are given.

Oxygen difluoride
See Oxygen difluoride: Halogens

Oxygen, Polymers
Groome, I. J., *Chem. Brit.*, 1983, **19**, 644—665
Bromination of polymers should be effected at temperatures below 120°C to avoid the possibility of explosion likely at higher temperatures if traces of oxygen were present in the highly unsaturated pyrolysis products.

Ozone
See Ozone: Bromine

Phosphorus

1. Bandar, L. S. *et al., Zh. Prikl. Khim.*, 1966, **39**, 2304
2. ‘Leaflet No. 2’, Inst. of Chem., London, 1939

During preparation of hydrogen bromide by addition of bromine to a suspension of red phosphorus in water, the latter must be freshly prepared to avoid the possibility of explosion. This is due to formation of peroxides in the suspension on standing and subsequent thermal decomposition [1]. In the earlier description of such an explosion, action of bromine on boiling tetralin was preferred to generate hydrogen bromide [2], which is now available in cylinders.

Rubber
Pascal, 1960, Vol. 16.1, 371
Bromine reacts violently in contact with natural rubber, but more slowly with some synthetic rubbers.

Sodium hydroxide
MCA Case History No. 1636
A bucket containing 25% sodium hydroxide solution was used to catch and neutralise bromine dripping from a leak. Lack of stirring allowed a layer of unreacted bromine to form below the alkali. Many hours later, a violent eruption occurred when the layers were disturbed during disposal operations. Continuous stirring is essential to prevent stratification of slowly reacting mutually insoluble liquids, especially of such differing densities.

Tetracarbonylnickel
See Tetracarbonylnickel: Bromine

Tetrahydrofuran

Tinley, E. J., private comm., 1983

Rapid addition of bromine to the dried solvent to make a 10% solution caused a vigorous reaction with gas evolution. As this happened in a newly installed brightly illuminated fume cupboard lined with a reflective white finish, photocatalysed bromination of the solvent may have been involved, as has been observed in chlorine—ether systems.

See Diethyl ether, above; Chlorine: Diethyl ether

Tetraselenium tetranitride

See Tetraselenium tetranitride: Alone, or Halogens

Trialkyl boranes

Coates, 1967, Vol. 1, 199

The lower homologues tend to ignite in bromine or chlorine.

Trimethylamine

Bohme, H. *et al., Chem. Ber.*, 1951, **84**, 170—181

The 1:1 adduct (presumably *N*-bromotrimethylammonium bromide) decomposes explosively when heated in a sealed tube.

Trioxygen difluoride

See ‘Trioxygen difluoride’: Various materials

Tungsten, Tungsten trioxide

Tillack, J., *Inorg. Synth.*, 1973, **14**, 116—120

During preparation of tungsten(IV) dibromide oxide, appropriate proportions of reactants are heated in an evacuated sealed glass ampoule to 400—500°C. Initially only one end should be heated to prevent excessive pressure bursting the ampoule.

See other GLASS INCIDENTS, HALOGENS, OXIDANTS

0262. Calcium bromide

[7789-41-5] **Br_2Ca**

Br—Ca—Br

Potassium

See Potassium: Metal halides

See other METAL HALIDES

0263a. Cobalt(II) bromide

[7789-43-7] **Br_2Co**

Br—Co—Br

Sodium

See Sodium: Metal halides

See other METAL HALIDES

0263b. Tetraamminecopper(II) bromate

[ ] **$Br_2CuH_{12}N_4O_6$**

$(NH_3)_4Cu^{2+}\ 2BrO_3^-$

Rammelsberg, C. F., *Pogg. Ann*, 1842, **55**, 63
A bright blue solid detonating at 140°C or if struck.
See other AMMINEMETAL OXOSALTS

0264. Copper(I) bromide

[7787-70-4] **Br_2Cu_2**

Br—Cu—Cu—Br

tert-Butyl peroxybenzoate, Limonene
See tert-Butyl peroxybenzoate: Copper(I) bromide, etc.
See other METAL HALIDES, REDUCANTS

0265. Iron(II) bromide

[7789-46-0] **Br_2Fe**

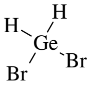
Br—Fe—Br

Potassium
See Potassium: Metal halides

Sodium
See Sodium: Metal halides
See other METAL HALIDES

0266. Dibromogermane

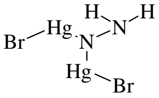
[13769-36-3] **Br_2GeH_2**



Preparative hazard
See Bromine: Germane
See related METAL HALIDES, METAL HYDRIDES

0267. *N,N*-Bis(bromomercurio)hydrazine

[ ] **$Br_2H_2Hg_2N_2$**



Hofmann, K. A. *et al., Ann.*, 1899, **305**, 217
An explosive compound.
See other MERCURY COMPOUNDS, *N*-METAL DERIVATIVES

0268. Mercury(II) bromide

[7789-47-1] **Br_2Hg**

$Br{-}Hg{-}Br$

HCS 1980, 614

Indium

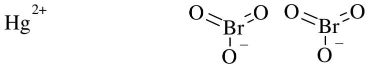
Clark, R. J. *et al., Inorg. Synth.*, 1963, **7**, 19—20

Interaction at 350°C is so vigorous that it is unsafe to increase the scale of this preparation of indium bromide.

See other MERCURY COMPOUNDS, METAL HALIDES

0269. Mercury(II) bromate

[26522-91-8] (dihydrate) **Br_2HgO_6**



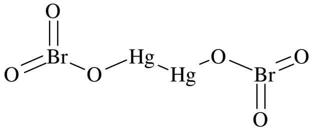
Janz, 1976, Table 2, 7

It deflagrates around 155°C.

See other MERCURY COMPOUNDS, METAL OXOHALOGENATES, OXIDANTS

0270. Mercury(I) bromate

[13465-33-3] **$Br_2Hg_2O_6$**



Hydrogen sulfide

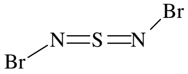
Pascal, 1960, Vol. 13.1, 1004

Contact of the gas with the solid oxidant causes ignition.

See other MERCURY COMPOUNDS, METAL HALOGENATES

0271. *N,N′*-Dibromosulfurdiimide

[ ] **Br_2N_2S**



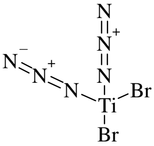
Seppelt, K. *et al., Angew. Chem. (Int.)*, 1969, **8**, 771

This is more shock sensitive than the iodo- analogue, which explodes both on melting and impact. The chloro-compound is not known.

See other *N*-HALOGEN COMPOUNDS, N—S COMPOUNDS

0272. Titanium diazide dibromide

[32006-07-8] **Br_2N_6Ti**



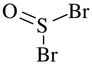
Dehnicke, K., *Angew. Chem. (Intern.Ed.)*, 1979, **18**, 507: *Chem. Ztg.*, 1982, **106**, 187—188

A highly explosive solid, (possibly polymeric).

See other METAL AZIDE HALIDES

0273. Sulfinyl bromide (Thionyl bromide)

[507-16-4] **Br_2OS**



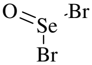
1. Hodgson, P. K. G., private comm., 1981
2. Beattie, T. R., *Chem. Eng. News*, 1982, **60**(28), 5

Opening an unused but old commercial ampoule of the ice-cooled bromide led to eruption of the decomposed contents [1]. Similar occurrences on 2 occasions were reported later [2], though on both occasions hexabromonaphthalene was identified in the residue (suggesting contamination of the bromide by naphthalene as an additional source of internal pressure). Sulfinyl bromide is of limited stability, decomposing to sulfur, sulfur dioxide and bromine, and so should be stored under refrigeration and used as soon as possible.

See other GAS EVOLUTION INCIDENTS, NON-METAL HALIDES

0274. Seleninyl bromide

[7789-51-7] **Br_2OSe**



Metals

Mellor, 1947, Vol. 10, 912

Sodium and potassium react explosively (the latter more violently), and zinc dust ignites, all in contact with the liquid bromide.

See Sodium: Non-metal halides

Phosphorus

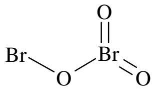
Mellor, 1947, Vol. 10, 912

Red phosphorus ignites, and white phosphorus explodes, in contact with the liquid bromide.

See other NON-METAL HALIDES

0275. Bromine bromate (Dibromine trioxide)

[152172-79-1] **Br_2O_3**



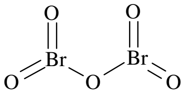
Kuschel, R. *et al., Angew. Chem. (Int.)*, 1993, **32**(11), 1632

Orange needles which decompose above —40°C and detonate if warmed rapidly to 0°C. The isomeric bromous anhydride would not be expected to be much more stable.

See other HALOGEN OXIDES

0276. Dibromine pentoxide

[58572-43-3] **Br_2O_5**



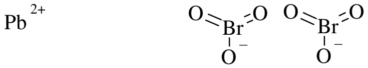
Leopold, D. *et al., Angew. Chem. (Int.),* 1994, **33**(9), 975

The yellow powder decomposes above −40°C, sometimes by detonation.

See other HALOGEN OXIDES

0277. Lead bromate

[34018-28-5] **Br_2O_6Pb**



Sidgwick, 1950, 1227

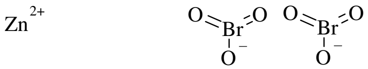
An explosive salt.

See Lead acetate—lead bromate

See other HEAVY METAL DERIVATIVES, METAL HALOGENATES

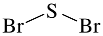
0278. Zinc bromate

[14519-07-4] **Br_2O_6Zn**



See entry METAL HALOGENATES

0279. Sulfur dibromide
[14312-20-0] **Br_2S**



Nitric acid

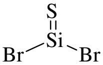
See Nitric acid: Sulfur halides

Sodium

See Sodium: Non-metal halides

See other NON-METAL HALIDES

0280. Silicon dibromide sulfide
[13520-74-6] **Br_2SSi**



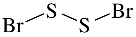
Water

Bailar, 1973, Vol. 1, 1415

Hydrolysis of the sulfide is explosive.

See related NON-METAL HALIDES, NON-METAL SULFIDES

0281. Disulfur dibromide
[13172-31-1] **Br_2S_2**



HCS 1980, 873

Metals

1. Mellor, 1947, Vol. 10, 652
2. Pascal, 1960, Vol. 13.2, 1162

Thin sections of potassium or sodium usually ignite in the liquid bromide. Iron at about 650°C ignites and incandesces in the vapour [1]. Interaction with finely divided aluminium or antimony is violent [2].

Oxidants

Taradoire, F., *Bull. Soc. Chim. Fr.*, 1945, **12**, 95

Interaction with moist barium bromate is very violent, and mixtures with potassium bromate and water (3—4%) ignite at 20°C. In absence of water, ignition occurs at 125°C. Silver bromate also deflagrates.

See Silver bromate: Sulfur compounds

Nitric acid: Sulfur halides

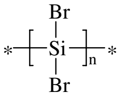
Phosphorus

See Phosphorus: Non-metal halides

See other NON-METAL HALIDES

0282. Poly(dibromosilylene)

[14877-32-8] **$(Br_2Si)_n$**



Oxidants

Brauer, 1963, Vol. 1, 688

Ignites in air at 120°C and reacts explosively with oxidants such as nitric acid.

See related NON-METAL HALIDES

0283. Titanium dibromide

[13783-04-5] **Br_2Ti**

Br—Ti−Br

Gibson, 1969, 60—61

It may ignite in moist air.

See other METAL HALIDES, PYROPHORIC MATERIALS

0284. Zirconium dibromide

[24621-17-8] **Br_2Zr**

Br—Zr−Br

Air, or Water

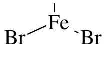
Pascal, 1963, Vol. 9, 558

It ignites in air, reacts violently with water and incandesces in steam.

See other METAL HALIDES, PYROPHORIC MATERIALS

0285. Iron(III) bromide

[10031-26-2] **Br_3Fe**



Potassium

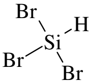
See Potassium: Metal halides

Sodium

See Sodium: Metal halides

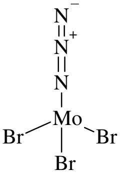
See other METAL HALIDES

†0286. Tribromosilane
[7789-57-3] **Br_3HSi**



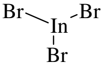
Schumb, W. C., *Inorg. Synth.*, 1939, **1**, 42
It usually ignites when poured in air (generating an extended liquid/air interface). This ignition is remarkable in a compound containing over 89% of bromine.
See other HALOSILANES

0287. Molybdenum azide tribromide
[68825-98-9] **Br_3MoN_3**



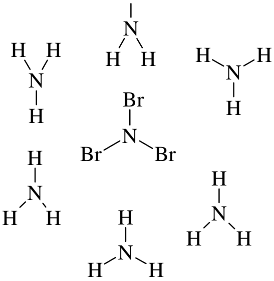
Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 510
It is highly explosive.
See other METAL AZIDE HALIDES

0288. Indium bromide
[13645-09-3] **Br_3In**



Preparative hazard
See Mercury(II) bromide: Indium
See other METAL HALIDES

0289. Nitrogen tribromide hexaammoniate (Tribromamine hexaammoniate)
[ ] **$Br_3N.6H_3N$**



Alone, or Non-metals

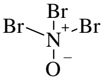
Mellor, 1967, Vol. 8, Suppl. 2, 417; 1940, Vol. 8, 605

The compound, formed by condensation of its vapour at —95°C explodes suddenly at —67°C. Prepared in another way, it is stable under water but explodes violently in contact with phosphorus or arsenic.

See other *N*-HALOGEN COMPOUNDS

0290. Tribromamine oxide (Nitrosyl tribromide)

[13444-89-8] **Br_3NO**



Sodium—antimony alloy

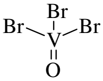
Mellor, 1940, Vol. 8, 621

The powdered alloy ignites when dropped into the vapour.

See other *N*-HALOGEN COMPOUNDS, *N*-OXIDES

0291. Vanadium tribromide oxide

[13520-90-6] **Br_3OV**



Water

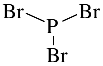
Bailar, 1973, Vol. 3, 508

The bromide (and analogous chloride) is violently hygroscopic.

See related METAL HALIDES

0292. Phosphorus tribromide

[7789-60-8] **Br_3P**



HCS 1980, 744

Calcium hydroxide, Sodium carbonate

Seager, J. F., *Chem. Brit.*, 1976, **12**, 105

During disposal of the tribromide by a recommended procedure involving slow addition to a mixture of soda ash and dry slaked lime, a violent reaction, accompanied by flame, occurred a few seconds after the first drop. Cautious addition of the bromide to a large volume of ice water is suggested for disposal.

Hydrazine derivatives

Coogan, M. P., *Chem. Brit.*, 2000, **36**(5), 22

Reaction of a diacylhydrazine under nitrogen produced a gas pyrophoric at the vent to atmosphere. It is postulated that the hydrazine moiety reduced the phosphorus tribromide to a volatile phosphine.

Oxidants

See Chromyl chloride: Non-metal halides
Oxygen (Gas): Phosphorus tribromide
Ruthenium(VIII) oxide: Phosphorus tribromide

3-Phenylpropanol

Taylor, D. A. H., *Chem. Brit.*, 1974, **10**, 101—102

During dropwise addition of the bromide to the liquid alcohol, the mechanical stirrer stopped, presumably allowing a layer of the dense tribromide to accumulate below the alcohol. Later manual shaking caused an explosion, probably owing to the sudden release of gaseous hydrogen bromide on mixing.

See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS

Potassium

See Potassium: Non-metal halides

Sodium, Water

See Sodium: Non-metal halides

Sulfur acids

Dillon, K. B. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 885—887

The tribromide is initially insoluble in 100% sulfuric acid, 25% oleum or fluorosulfuric acid, but violent exotherms occurred after contact for 11, 4 and 5 hours respectively. 65% Oleum reacts violently on contact, and chlorosulfuric acid vigorously after shaking.

See Phosphorus trichloride: Sulfur acids
Phosphorus triiodide: Sulfur acids

See other INDUCTION PERIOD INCIDENTS

1,1,1-Tris(hydroxymethyl)methane

1. Derfer, J. M. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 175
2. Farber, S. *et al., Synth. Comm.*, 1974, **4**, 243

Interaction to form the corresponding tribromomethyl compound is extremely hazardous, even using previously specified precautions [1]. Several fires occurred in the effluent gases, and in reaction residues exposed to air [2], doubtless owing to phosphine or its derivatives.

Water

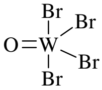
Mellor, 1940, Vol. 8, 1032

Interaction with warm water is very rapid and may be violent with limited quantities.

See other NON-METAL HALIDES

0293. Tungsten tetrabromide oxide

[13520-77-9] **Br_4OW**



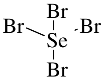
Preparative hazard

See Boron tribromide: Tungsten trioxide

See related METAL HALIDES

0294. Selenium tetrabromide

[7789-65-3] **Br_4Se**



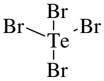
Trimethylsilyl azide

See Trimethylsilyl azide: Selenium halides

See other NON-METAL HALIDES

0295. Tellurium tetrabromide

[10031-27-3] **Br_4Te**



Ammonia

Sorbe, 1968, 154

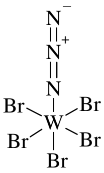
Interaction gives a mixture of ‘tritellurium’ tetranitride and tellurium bromide nitride, which explodes on heating.

See Tetratellurium tetranitride

See other METAL HALIDES

0296. Tungsten azide pentabromide

[ ] **Br_5N_3W**



Extremely explosive.

See entry METAL AZIDE HALIDES

0297. Carbon

[7440-44-0] (Amorphous) C_n
[7782-42-5] (Graphite) C_n
[99685-96-8] (Fullerene) C_{60}, C_{70}
[115383-22-7] [7782-40-3] (Diamond) C_n
[126487-10-3] (Cyclooctadecanonayne) C_{18}

C

1. Anon., *Fire Prot. Assoc. J.*, 1964, 337
2. Cameron, A. *et al., J. Appl. Chem.*, 1972, **22**, 1007
3. Zav'yalov, A. N. *et al., Chem. Abs.*, 1976, **84**, 166521
4. Suzuki, E. *et al., Chem. Abs.*, 1980, **93**, 78766
5. Beever, P. F., *Runaway Reactions*, 1981, Paper 4/X, 1—9
6. Van Liempt, J. H. M., *PT-Procestech.* (Neth.), 1988, **43**(9), 45—47
7. Anon., *Loss Prev. Bull.*, 1992, **105**, 15
8. Diederich, F. *et al, Angewand. Chem. (Int.)*, 1994, **33**(9), 997
9. Editor's comments
10. Hyun, S. H. *et al., J. Appl. Fire Sci.*, 1999, **8**(3), 219
11. Hofelich, T. C. *et al, Chem. Engineering*, 2000, (1), 99
12. Dagani, R., *Chem. Eng. News*, 2002, **80**(17), 9

Activated carbon exposed to air is a potential fire hazard because of its very high surface area and adsorptive capacity. Freshly prepared material may heat spontaneously in air, and presence of water accelerates this. Spontaneous heating and ignition may occur if contamination by drying oils or oxidising agents occurs [1]. The spontaneous heating effect has been related to the composition and method of preparation of activated carbon, and the relative hazards may readily be assessed [2]. Free radicals present in charcoal are responsible for auto-ignition effects, and charcoal may be stabilised for storage and transport without moistening by treatment with hot air at 50°C [3]. The causes of accidents involving activated carbon have been surveyed [4]. Fires originating in paper-bagged cargoes of active carbon in holds of ships travelling through tropical waters have been investigated by isothermal methods. Use of oxygen-impermeable plastic bags to limit oxidation and moisture uptake was proposed as a solution to the problem [5]. The potential hazards arising from use of activated carbon for various purposes are reviewed. Hazards usually arise from self-heating from adsorption of vapours or gases (especially oxygen), and may lead to autoignition, fire or explosions, including carbon dust explosions [6]. A fire in an activated charcoal odour abatement system, essentially caused by scale-up without considering the reduced heat loss thus occasioned, is reported [7]. The higher the internal suface of activated carbon powder, the greater the dust explosion pressure. Fresh is more dangerous than used material. Use of carbon beds in cryogenic applications introduces the danger of selective absorption of liquid oxygen, forming a powerful explosive [10]. Advice on calorimetrically evaluating carbon beds to prevent overheating leading to fire is given, it concentrates on oxidation of adsorbed volatiles, rather than the carbon itself [11].

Fullerenes may be expected to be at least as autoxidisable as charcoal (graphite) when suitably finely divided. Heats of formation (solid, w.r.t. graphite): C_{60} 3.2 kJ/g; C_{70} 3.0 kJ/g. They have hitherto proved surprisingly stable kinetically [8]. The cyclic C_{18}, when available in substantial quantity, will surely prove capable of spontaneous combustion and will probably be explosive [9]. Single cell carbon nanotubes ignite on exposure to photographic flash [12].

Generation of pyrophoric carbon
See Barium acetylide
See Helium
See also HIGH SURFACE-AREA SOLIDS, PETROLEUM COKE

Alkali metals
1. Bailar, 1973, Vol. 1, 443
2. Werner, H. *et al., Fullerene Sci. Technol.*, 1993, **1**(2), 199

Graphite in contact with liquid potassium, rubidium or caesium at 300°C gives intercalation compounds (C_8M) which ignite in air and may react explosively with water [1]. 'Fullerene black' — probably a finely divided and distorted graphite — impregnated with potassium explodes spontaneously in air [2].
See Potassium: Carbon
Sodium: Non-metals

Chlorinated paraffins, Lead(IV) oxide, Manganese(IV) oxide
See Lead(IV) oxide: Carbon black, etc.

1,4-Diazabicyclo[2.2.2]octane
Hardman, J. S. *et al., Fuel*, 1980, **59**, 213—214
Activated carbon showed an auto-ignition temperature in flowing air of 452—518°C. Presence of 5% of the base ('triethylenediamine') adsorbed on the carbon reduced the AIT to 230—260°C. At high air flow rates an exotherm was seen at 230—260°, but ignition did not then occur until 500°C.

Dibenzoyl peroxide
See Dibenzoyl peroxide: Charcoal

Iron(II) oxide, Oxygen (Liquid)
See Oxygen (Liquid): Carbon, Iron(II) oxide

Lithium, Lithium tetrachloroaluminate, Sulfinyl chloride
See Lithium: Carbon, etc.

Metal salts
MCA Case History No. 1094
Dry metal-impregnated charcoal catalyst was being added from a polythene bag to an aqueous solution under nitrogen. Static so generated ignited the charcoal dust and caused a flash fire. The risk was eliminated by adding a slurry of catalyst in water from a metal container.
See Cobalt(II) nitrate: Carbon
See other STATIC INITIATION INCIDENTS

Molybdenum(IV) oxide
See Molybdenum(IV) oxide: Graphite

2-Nitrobenzaldehyde
See 2-Nitrobenzaldehyde: Active carbon

Nitrogen oxide, Potassium hydrogen tartrate
See Nitrogen oxide: Carbon, Potassium hydrogen tartrate

Other reactants
Yoshida, 1980, 225
MRH values calculated for 25 combinations with oxidants are given.

Oxidants MRH values show % of carbon

Carbon has frequently been involved in hazardous reactions, particularly finely divided or high-porosity forms exhibiting a high ratio of surface area to mass (up to 2000 m^2/g). It then functions as an unusually active fuel which possesses adsorptive and catalytic properties to accelerate the rate of energy release involved in combustion reactions with virtually any oxidant. Less active forms of carbon will ignite or explode on suitably intimate contact with oxygen, oxides, peroxides, oxosalts, halogens, interhalogens and other oxidising species. Individual combinations are found under the entries listed below.

Ammonium perchlorate: Carbon	MRH 6.19/85
Bromine pentafluoride: Acids, etc.	
Bromine trifluoride: Halogens, etc.	
Chlorine trifluoride: Metals, etc.	
Cobalt(II) nitrate: Carbon	MRH 3.68/86
Dichlorine oxide: Carbon, or: Oxidisable materials	MRH 5.14/90
Fluorine: Non-metals	
Hydrogen peroxide: Carbon	MRH 6.19/15
Iodine heptafluoride: Carbon	
Iodine(V) oxide: Non-metals	
Nitrogen oxide: Non-metals	MRH 7.82/16
Nitrogen trifluoride: Charcoal	
Oxygen difluoride: Non-metals	
Oxygen (Liquid): Charcoal	MRH (Gas) 8.95/27
Ozone: Charcoal, Potassium iodide	
Peroxyformic acid: Non-metals	MRH 5.69/tr.
Peroxyfuroic acid: Alone, etc,	
Potassium chlorate: Charcoal, etc.	MRH 4.52/87
Potassium dioxide: Carbon	
Potassium nitrate: Non-metals	
Potassium permanganate: Non-metals	MRH 2.59/7
Silver nitrate: Non-metals	MRH 2.47/10
Sodium nitrate: Non-metals	
Sodium peroxide: Non-metals	MRH 2.30/7
‘Trioxygen difluoride’: Various materials	
Zinc nitrate: Carbon	MRH 3.86/87

Potassium hydroxide

Hejduk, J., *Chem. Abs.*, 1989, **110**, 107229

Analytical decomposition of powdered diamond by fusion with potassium hydroxide may become explosive. This can be avoided by fusion with a potassium carbonate—sodium carbonate mixture, followed by addition of small portions of potassium nitrite or nitrate.

Sodium hydrogen carbonate

See Sodium hydrogen carbonate: Carbon, Water

Sodium tetrahydroborate

See Sodium tetrahydroborate

Turpentine

1. US Environmental Protection Agency, *Alert EPA 550-F-97-002e*, 1997
2. US Environmental Protection Agency, *EPA 550-R-98-003*, 1998
3. Woodward, J. L. *et al., Proceedings 36th Annual Loss Prevention Symposium*, 2002, 3

Fires have been caused when using activated carbon to de-odorise crude sulfate turpentine. This is another case of adsorption forming hot spots then exposed to air [1]. A full report on the major incident which directly triggered the above alert appeared later. Initial heating of the carbon adsorber is blamed upon adsorption of sulphur compounds. This raised the bed, not adequately protected from air inflow, to a temperature sufficient for ignition of turpentine itself. [In view of the easy autoxidation of most volatile organic sulphur compounds, there may have been an intermediate step – Ed.]. Adjacent tanks breached by the consequent fire contained aqueous sodium hydrosulfide and an acid cleaning solution, which mixed and reacted, liberating extremely noxious hydrogen sulfide [2]. The incident is further covered in [3].

Unsaturated oils

1. Bahme, C. W., *NFPA Quart.*, 1952, **45**, 431
2. von Schwartz, 1918, 326

Unsaturated (drying) oils, like linseed oil, etc., will rapidly heat and ignite when distributed on active carbon, owing to the enormous increase in surface area of the oil exposed to air, and in the rate of oxidation, probably catalysed by metallic impurities [1]. A similar, but slower, effect occurs on fibrous materials such as cotton waste [2].

See other CATALYTIC IMPURITY INCIDENTS, NON-METALS

0298. Silver cyanide

[506-64-9] **CAgN**

$$Ag^{+} \quad {}^{-}C{\equiv}N$$

Fluorine

See Fluorine: Metal salts

See other ENDOTHERMIC COMPOUNDS, METAL CYANIDES, SILVER COMPOUNDS

Phosphorus tricyanide

See Phosphorus tricyanide (reference 2)

0299. Silver cyanate

[3315-16-0] **CAgNO**

$$\mathrm{Ag^{+}} \qquad \overset{-}{\mathrm{O}}-\!\!\!\equiv\mathrm{N}$$

Sorbe, 1968, 125

It explodes on heating.

See other SILVER COMPOUNDS

See related METAL CYANIDES (AND CYANO COMPLEXES)

0300. Silver fulminate

[5610-59-3] **CAgNO**

$$\mathrm{Ag^{+}} \qquad \overset{-}{\mathrm{C}}\equiv\overset{+}{\mathrm{N}}-\mathrm{O^{-}}$$

1. Urbanski, 1967, Vol. 3, 157
2. Collins, P. H. *et al., Propellants, Explos.*, 1978, **3**, 159—162

Silver fulminate is dimeric and rather endothermic (ΔH_f° +361.5 kJ/dimol, 1.21 kJ/g). It is readily formed from silver or its salts, nitric acid and ethanol, and is a much more sensitive and powerful detonator than mercuric fulminate [1]. The properties and applications have been reviewed [2].

Hydrogen sulfide

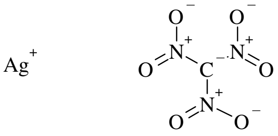
Boettger, A., *J. Pr. Chem.*, 1868, **103**, 309

Contact with hydrogen sulfide at ambient temperature initiates violent explosion of the fulminate.

See other ENDOTHERMIC COMPOUNDS, METAL FULMINATES, SILVER COMPOUNDS

0301. Silver trinitromethanide

[25987-94-4] **$CAgN_3O_6$**



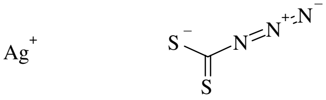
Witucki, E. F. *et al., J. Org. Chem.*, 1972, **37**, 152

The explosive silver salt may be replaced with advantage by the potassium salt in the preparation of 1,1,1-trinitroalkanes.

See other POLYNITROALKYL COMPOUNDS, SILVER COMPOUNDS

0302. Silver azidodithioformate

[74093-43-9] **$CAgN_3S_2$**



Sorbe, 1968, 126

The tetrahydrated salt explodes on the slightest friction.

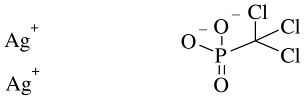
See Azidodithioformic acid

See other SILVER COMPOUNDS

See related ACYL AZIDES

0303. Silver trichloromethanephosphonate

[ ] **$CAg_2Cl_3O_3P$**



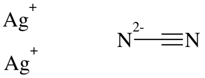
Yakubovich, A. Ya. *et al., Chem. Abs.*, 1953, **47**, 2685i

It explodes on heating.

See other SILVER COMPOUNDS

0304. Disilver cyanamide

[3384-87-0] **CAg_2N_2**



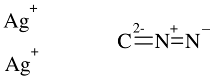
1. Chrétien, A. *et al., Compt. rend.*, 1951, **232**, 1114
2. Deb, S. K. *et al., Trans. Faraday Soc.*, 1959, **55**, 106—113
3. Cradock, S., *Inorg. Synth.*, 1974, **15**, 167

During pyrolysis to silver (via silver dicyanamide), initial heating must be slow to avoid explosion [1]. High intensity illumination will also cause explosive decomposition of a confined sample [2]. Safety precautions for preparation and subsequent use of the explosive salt are detailed [3].

See other IRRADIATION DECOMPOSITION INCIDENTS, *N*-METAL DERIVATIVES, SILVER COMPOUNDS

0305. Disilver diazomethanide

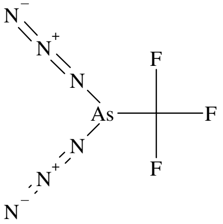
[54086-40-7] **CAg_2N_2**



Blues, E. T. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 466—467
Both the disilver derivative and its precursory dipyridine complex are highly explosive and extremely shock-sensitive when dry.
See other DIAZO COMPOUNDS, SILVER COMPOUNDS

0306. Diazido(trifluoromethyl)arsine

[157951-76-3] **$CAsF_3N_6$**



Ang, H. G. *et al., Inorg. Chem.*, 1994, **33**(20), 4425
A vapour phase study of this azide showed it sometimes to explode when exposed to heat.
See other AZIDES

0307. Gold(I) cyanide

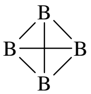
[506-65-0] **CAuN**

$Au^+ \quad \overset{-}{C}\equiv N$

Magnesium
See Magnesium: Metal cyanides
See other GOLD COMPOUNDS, METAL CYANIDES

0308. Carbon tetraboride

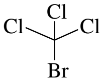
[12069-32-8] **CB_4**



Chlorine trifluoride
See Chlorine trifluoride: Boron-containing materials
See related NON-METALS

0309. Bromotrichloromethane

[75-62-7] **$CBrCl_3$**



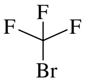
Ethylene

See Ethylene: Bromotrichloromethane

See other HALOALKANES

0310. Bromotrifluoromethane

[75-63-8] **$CBrF_3$**



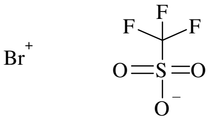
Aluminium

See Aluminium: Halocarbons

See other HALOALKANES

0311. Bromine(I) trifluoromethanesulfonate

[70142-16-4] **$CBrF_3O_3S$**



Readily oxidisable materials

Katsuhara, Y. *et al., J. Org. Chem.*, 1980, **45**, 2442

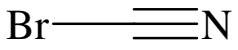
Contact of this oxidant with readily oxidisable materials may lead to explosions.

See Chlorine(I) trifluoromethanesulfonate

See related HYPOHALITES

0312. Cyanogen bromide

[506-68-3] **CBrN**



HCS 1980, 338

1. Grossman, M. I., *Chem. Eng. News*, 1980, **58**(35), 43
2. Harvey, W. R. *et al., Chem. Eng. News*, 1981, **59**(5), 49
3. Crocker, H. P., *Chem. Eng. News*, 1981, **59**(5), 49

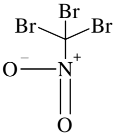
Cyanogen bromide is moderately endothermic (ΔH_f° (g) +50 kJ/mol, 0.47 kJ/g) and shows evidence of instability. The plastic cap of a bottle stored in a laboratory for several years on a high shelf, occasionally at 31°C, shattered and drove fragments into the shelf above [1]. This instability was confirmed, and a procedure outlined to obviate the use of the bromide in autoanalysis by generating cyanogen chloride on demand from Chloramine-T and potassium cyanide [2]. A 50 wt% solution of the bromide in chloroform is a stable and convenient form for use [3].

See Cyanogen chloride

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

0313. Tribromonitromethane

[464-10-8] **CBr_3NO_2**



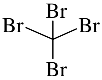
Sorbe, 1968, 40

It is used as an explosive.

See related NITROALKANES

0314. Carbon tetrabromide (Tetrabromomethane)

[558-13-4] **CBr_4**



HCS 1980, 283

Hexacyclohexyldilead

See Hexacyclohexyldilead: Halocarbons

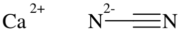
Lithium

See Lithium: Halocarbons

See other HALOALKANES

0315. Calcium cyanamide

[156-62-7] **$CCaN_2$**



Water

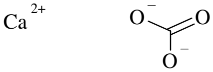
Pieri, M., *Chem. Abs.*, 1952, **46**, 8335i

Absorption of water during handling or storage of technical calcium cyanamide may cause explosions, owing to liberation of acetylene from the calcium carbide content (up to 2%). Precautions are discussed.

See other CYANO COMPOUNDS, *N*-METAL DERIVATIVES

0316. Calcium carbonate

[471-34-1] **$CCaO_3$**



HCS 1980, 265

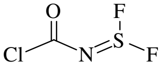
Fluorine

See Fluorine: Metal salts

See other INORGANIC BASES

0317. (Chlorocarbonyl)imidosulfur difluoride

[53654-97-0] **$CClF_2NOS$**



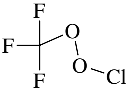
Mews, R. *et al., Inorg. Synth.*, 1986, **24**, 14—16

The title compound, particularly if impure, rapidly forms explosive decomposition products when stored at ambient temperature.

See other ACYL HALIDES, N—S COMPOUNDS

0318a. Chloroperoxytrifluoromethane

[32755-26-3] **$CClF_3O_2$**



Tetrafluoroethylene

Ratcliffe, C. T. *et al., J. Amer. Chem. Soc.*, 1971, **93**, 3887—3888

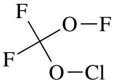
The peroxy compound initiated explosive polymerisation of tetrafluoroethylene when a mixture prepared at —196°C warmed to —110°C.

See other ORGANIC PEROXIDES, POLYMERISATION INCIDENTS

See related HYPOHALITES

0318b. Chloroxyfluoroxydifluoromethane (Chloroxydifluoromethyl hypofluorite)

[150905-41-2] **$CClF_3O_2$**



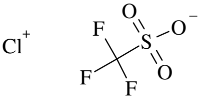
Russo, A. *et al., Inorg. Chem.*, 1995, **34**(24), 6221

This compound, prepared at liquid nitrogen temperatures, was found to undergo mildly explosive decomposition when its vapour pressure passed 50 millibar. The boiling point was not determinable.

See other HYPOHALITES

0319. Chlorine(I) trifluoromethanesulfonate

[65597-24-2] **$CClF_3O_3S$**



Readily oxidisable materials

1. Katsuhara, Y. *et al., J. Amer. Chem. Soc.*, 1979, **101**, 1040
2. Katsuhara, Y. *et al., J. Org. Chem.*, 1980, **45**, 2442

Contact of the oxidant with readily oxidisable materials must be controlled and at low temperatures to prevent explosions.

See Bromine(I) trifluoromethanesulfonate

See related HYPOHALITES

0320. Trifluoromethyl perchlorate

[52003-45-9] **$CClF_3O_4$**

Preparative hazard

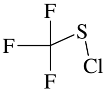
1. Schack, C.J. *et al., Inorg. Chem.*, 1974, **13**, 2375
2. Schack, C.J. *et al., Inorg. Nucl. Chem. Lett.*, 1974, **10**, 449

Though apparently not explosively unstable [1], its synthesis [2] was occasionally accompanied by deflagrations.

See other ALKYL PERCHLORATES

0321. Trifluoromethanesulfenyl chloride

[421-17-0] **$CClF_3S$**



Chlorine fluorides

Sprenger, G. H. *et al., J. Fluorine Chem.*, 1976, **7**, 335

In the preparation of trifluoromethylsulfur trifluoride, the chloride must be dissolved in a fully halogenated solvent to prevent explosion during treatment with chlorine fluoride or chlorine trifluoride.

See other HALOGENATION INCIDENTS

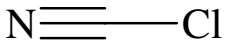
Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

See other ACYL HALIDES

0322. Cyanogen chloride

[506-77-4] **CClN**



HCS 1980, 339

Preparative hazard

Good, R. J., private comm., 1979

Crude cyanogen chloride (endothermic, prepared from hydrogen cyanide and chlorine) may trimerise violently to cyanuric chloride, catalysed by traces of hydrogen chloride or ammonium chloride.

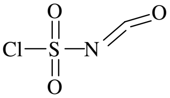
See Ammonium chloride

See Cyanogen bromide

See other CATALYTIC IMPURITY INCIDENTS, CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

0323a. Chlorosulfonyl isocyanate

[1189-71-5] **$CClNO_3S$**



Water

Graf, R., *Org. Synth.*, 1973, Coll. Vol. 5, 228

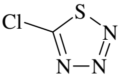
Interaction is violent.

See other ACYL HALIDES, N—S COMPOUNDS

See related CYANO COMPOUNDS

0323b. 5-Chloro-1,2,3,4-thiatriazole

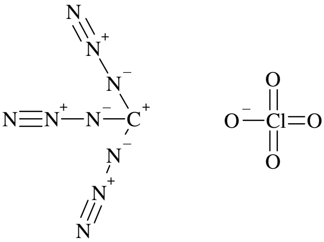
[88892-85-7] **$CClN_3S$**



See other THIATRIAZOLES

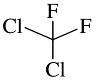
0324. Triazidocarbenium perchlorate (Triazidomethylium perchlorate)

[194093-98-6] **$CClN_9O_4$**



Petrie M. A. *et al., J. Amer. Chem. Soc.*, 1997, **119**, 8802
All salts of this cation were friction and shock sensitive, too sensitive for actual use as explosives. The most sensitive though, with estimated energy of 5.4 kJ/g, not the most powerful, was the perchlorate. Even though prepared on low milligram scale this invariably detonated spontaneously during work-up or soon after. The more powerful dinitramide (5.8 kJ/g) decomposed non-explosively on standing.
See other ORGANIC AZIDES

0325. Dichlordifluoromethane (Freon 12)
[75-71-8] **CCl_2F_2**

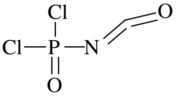


Aluminium
See Aluminium: Halocarbons

Magnesium
See Magnesium: Halocarbons

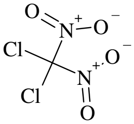
Water
See LIQUEFIED GASES: Water
See other HALOALKANES

0326. Phosphoryl dichloride isocyanate
[870-30-4] **CCl_2NO_2P**



Preparative hazard
See N-Carbomethoxyiminophosphoryl chloride
See related CYANO COMPOUNDS, NON-METAL HALIDES

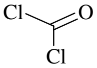
0327. Dichlorodinitromethane
[1587-41-3] **$CCl_2N_2O_4$**



Hocking, M. B. *et al., Chem. & Ind.*, 1976, 952
It exploded during attempted distillation at atmospheric pressure, but was distilled uneventfully at 31°C/13 mbar.
See other POLYNITROALKYL COMPOUNDS

0328. Carbonyl dichloride (Phosgene)

[75-44-5] **CCl_2O**



(*MCA SD-95*, 1967); *FPA H105*, 1981; *HCS 1980*, 740

Anon., *Sichere Chemiarb.*, 1988, **40**(3), 34
Trichloromethyl chloroformate (diphosgene) is used as a safe substitute for highly toxic phosgene gas. The latter is generated in situ by addition of catalytic amounts of tertiary amines or amides, or active carbon. Diphosgene also disproportionates to 2 equivalents of phosgene on heating above 250°C.

N,N-Dimethylbenzeneamine, Water
Anon., *J. Loss Prev.*, 1994, **7**(3), 257
The aniline was being phosgenated in toluene as solvent, the reaction ran wild and ejected more than 3 tonnes of reactor contents. This is believed to have been due to water contamination, possibly as ice. An initial charge of only part of the phosgene failed to show the exotherm anticipated if water was present, however this may not have been enough, nor was the thermocouple immersed in the solvent.
See Diprotium monoxide

Hexafluoroisopropylideneaminolithium
See Hexafluoroisopropylideneaminolithium: Non-metal halides

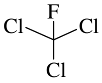
Other reactants
Yoshida, 1980, 341
MRH values for 18 combinations with a range of materials are given.

Potassium MRH 4.76/45
See Potassium: Non-metal halides

Sodium azide
See tert-Butyl azidoformate (reference 4)
See related ACYL HALIDES

0329. Trichlorofluoromethane (Freon 11)

[75-69-4] **CCl_3F**

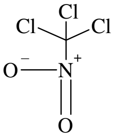


HCS 1980, 921

Metals

See Aluminium: Halocarbons
Barium: Halocarbons
Lithium: Halocarbons
METAL—HALOCARBON INCIDENTS
See other HALOALKANES

0330. Trichloronitromethane ('Chloropicrin')
[76-06-2] **CCl_3NO_2**



HCS 1980, 312

Anon., *Chem. Eng. News*, 1972, **50**(38), 13
Tests showed that above a critical volume, bulk containers of trichloronitromethane can be shocked into detonation. Containers below 700 kg content will now be the maximum size as against rail-tanks previously used.

Aniline
Jackson, K. E., *Chem. Rev.*, 1934, **14**, 269
Reaction at 145°C with excess aniline is violent.

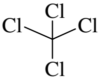
3-Bromopropyne
BCISC Quart. Safety Summ., 1968, **39**, 12
An insecticidal mixture in a rail-tank exploded with great violence during pump-transfer operations, possibly owing to the pump running dry and overheating. Both components of the mixture are explosive and the mixture was also found to be shock- and heat-sensitive.

Sodium hydroxide
Scholtz, S., *Explosivstoffe*, 1963, **11**, 159, 181
During destruction of chemical warfare ammunition, pierced shells containing chloropicrin reacted violently with alcoholic sodium hydroxide.

Sodium methoxide
Ramsey, B. G. *et al., J. Amer. Chem. Soc.*, 1966, **88**, 3059
During addition of the nitrocompound in methanol to sodium methoxide solution, the temperature must not be allowed to fall much below 50°C. If this happens, excess nitro compound will accumulate and cause a violent and dangerous exotherm.
See related NITROALKANES

0331. Carbon tetrachloride (Tetrachloromethane)

[56-23-5] **CCl_4**



(*MCA SD-3*, 1963); *HCS 1980*, 284; *RSC Lab. Hazard Data Sheet No. 59*, 1987

Aluminium chloride, Triethylaluminium
See Triethyldialuminium trichloride: Carbon tetrachloride

Aluminium oxide, Heavy metals
See Aluminium oxide: Halocarbons, etc.

Boranes
See BORANES: Carbon tetrachloride

Calcium disilicide
See Calcium disilicide: Carbon tetrachloride

Calcium hypochlorite
See Calcium hypochlorite: Carbon tetrachloride

Chlorine trifluoride MRH 1.21/44
See Chlorine trifluoride: Carbon tetrachloride

Decaborane(14)
See Decaborane(14): Ether, etc.

1,11-Diamino-3,6,9-triazaundecane (‘Tetraethylenepentamine’)

1. Hudson, F. L., private comm., 1973
2. Collins, R. F., *Chem. & Ind.*, 1957, 704

A mixture erupted vigorously one hour after preparation [1]. Interaction (not vigorous) of amines and halocarbons at ambient temperature had been recorded previously [2]. The presence of 5 basic centres in the viscous amine would be expected to enhance exothermic effects.

Dibenzoyl peroxide, Ethylene
See Ethylene: Carbon tetrachloride

Dibenzoyl peroxide: Carbon tetrachloride, Ethylene
See also WAX FIRE

Dimethylformamide MRH 1.30/28

1. ‘DMF Brochure’ Billingham, ICI, 1965
2. Cardillo, P. *et al., Ann. Chim.* (Rome), 1984, 74, 129—133

There is a potentially dangerous reaction of carbon tetrachloride with dimethylformamide in presence of iron. The same occurs with 1,2,3,4,5,6-hexachlorocyclohexane, but not with dichloromethane or 1,2-dichloroethane

under the same conditions [1]. A quantitative study of the reaction by DSC and ARC techniques shows that in a 1:1 wt. mixture with carbon tetrachloride in absence of iron, an exothermic reaction sets in below 100°C. Under adiabatic conditions, the heat release (207.6 J/g) would take a runaway reaction to over 240°C. In presence of 3% of iron powder, the same mixture shows 2 exotherms, one at 56°C (108 J/g) and the second at 94°C (275 J/g), a final adiabatic temperature exceeding 285°C being possible [2]. Dimethylacetamide behaves similarly but more so.
See N,N-Dimethylacetamide: Halogenated compounds
See other CATALYTIC IMPURITY INCIDENTS

Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Halocarbons

Ethanol (or methanol), Potassium sulfide
See Potassium dithioformate
See Sodium: Methanol and Sodium methoxide, both below

Fluorine
See Fluorine: Halocarbons

Metals	MRH values show % of carbon tetrachloride
See Aluminium: Halocarbons	MRH 4.14/81
Barium: Halocarbons	MRH 4.18/36
Beryllium: Halocarbons	
Lithium: Halocarbons	MRH 8.24/85
METAL—HALOCARBON INCIDENTS	
Potassium: Halocarbons	MRH 5.19/50
Potassium—sodium alloy: Halocarbons	
Sodium: Halocarbons	MRH 6.10/63
Uranium: Carbon tetrachloride	
Zinc: Halocarbons	MRH 2.43/54

Methanol
See Methanol: Carbon tetrachloride, Metals

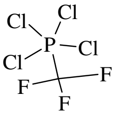
Other reactants
Yoshida, 1980, 148—149
MRH values for 23 combinations with a range of materials are given.

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

2-Propen-1-ol MRH 1.42/27
See 2-Propen-1-ol: Carbon tetrachloride
See other HALOALKANES

0332. Tetrachlorotrifluoromethylphosphorane

[1066-48-4] **CCl_4F_3P**



Tetramethyllead

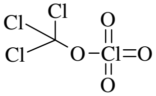
Yap, N. T. *et al., Inorg. Chem.*, 1979, **18**, 1304

Interaction under vacuum to form methyltrichlorotrifluoromethylphosphorane is hazardous, violent explosions having occurred twice after 30 min at ambient temperature.

See related ALKYLHALOPHOSPHINES

0333. Trichloromethyl perchlorate

[ ] **CCl_4O_4**



Sidgwick, 1950, 1236

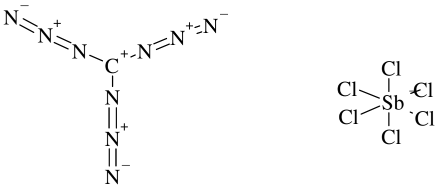
An extremely explosive liquid, only capable of preparation in minute amounts. Oxygen balance is 100%

See Silver perchlorate: Carbon tetrachloride

See other ALKYL PERCHLORATES

0334. Triazidomethylium hexachloroantimonate

[19708-47-5] **CCl_6N_9Sb**



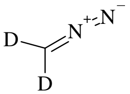
Müller, U. *et al., Angew. Chem.*, 1966, **78**, 825

The salt is sensitive to shock or rapid heating.

See related ORGANIC AZIDES

0335. Dideuterodiazomethane

[14621-84-2] **CD_2N_2**



Gassman, P. G. *et al., Org. Synth.*, 1973, **53**, 38—43

The explosive properties will be similar to those of diazomethane, for which precautions are extensively summarised.
See other DIAZO COMPOUNDS

0336. Poly(carbon monofluoride)

[25136-85-0] **$(CF)_n$**

Complex structure

Hydrogen

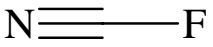
Bailar, 1973, Vol. 1, 1269
Above 400°C in hydrogen, deflagration and flaming of the polymer occurs, the vigour depending on the fluorine content. Rapid heating to 500°C in an inert atmosphere causes explosive deflagration.
See related HALOALKANES

Preparative hazard

See Fluorine: Graphite

0337a. Cyanogen fluoride

[1495-50-7] **CFN**

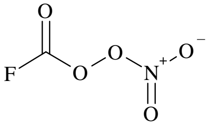


1. Bailar, 1973, Vol. 1, 1246
2. Fawcett, F. S. *et al., J. Amer. Chem. Soc.*, 1964, **86**, 2576

Cyanogen fluoride is a moderately endothermic compound, with $\Delta H_f^\circ(g)$ +35.8 kJ/mol, or 0.79 kJ/g. Polymerisation of cyanogen fluoride is rapid at ambient temperature and explosive in presence of hydrogen fluoride [1]. Cyanogen fluoride develops more pressure than would acetylene when initiated in the liquid phase at —41°C by a squib. At —80°C either hydrogen fluoride of boron trifluoride may initiate violent decomposition. The pure vapour is insensitive to sparks or igniters, but mixtures with air are more powerful than those of acetylene [2].
See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, POLYMERISATION INCIDENTS

0337b. Fluorocarbonylperoxonitrate

[ ] **$CFNO_5$**



Scheffler, D. *et al., Inorg. Chem.*, 1997, **36**(3), 339

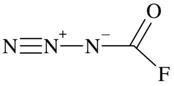
Preparation has been achieved; working with more than millimolar quantities is not advised. It is an explosive oxidant in contact with organics and can scarcely be safe in their absence.

See also Trifluoromethylperoxonitrate

See other PEROXYESTERS

0338. Azidocarbonyl fluoride (Fluorocarbonyl azide)

[23143-88-6] **CFN_3O**



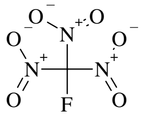
Mack, H.-G. *et al., J. Mol. Struct.,* 1994, **291**(2-3), 197

It is advised that the explosive gas be handled only in millimolar quantities and with due precautions.

See other ACYL AZIDES

0339. Fluorotrinitromethane

[1840-42-2] **CFN_3O_6**



Nitrobenzene

Zotov, E. V. *et al., Chem. Abs.*, 1980, **93**, 49732

Detonation characteristics of liquid explosive mixtures with nitrobenzene were studied.

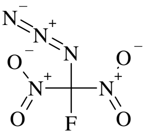
See other POLYNITROALKYL COMPOUNDS

Preparative hazard

See Fluorine: Trinitromethane

0340. Fluorodinitromethyl azide

[17003-82-6] **CFN_5O_4**



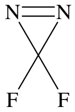
Unstable at ambient temperature.

See entry FLUORODINITROMETHYL COMPOUNDS

See other ORGANIC AZIDES, POLYNITROALKYL COMPOUNDS

0341. Difluorodiazirine

[693-85-6] **CF_2N_2**



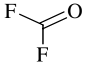
Craig, N. C. *et al., Spectrochim. Acta*, 1979, **35A**, 895

Explosive decomposition occurred during purification by GLC and when running the gas phase laser Raman spectrum.

See other DIAZIRINES, IRRADIATION DECOMPOSITION INCIDENTS

0342a. Carbonyl difluoride

[353-50-4] **CF_2O**



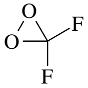
Hexafluoroisopropyldeneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

See related ACYL HALIDES

0342b. Difluorodioxirane

[96740-99-7] **CF_2O_2**



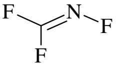
Russo, A. *et al., Angew. Chem. (Int.)*, 1993, **105**, 905

This is expected to be the most stable dioxirane, it has not shown itself to be explosive though not entirely stable. It is a potent oxidant. Such few others of the series as have been isolated are explosive.

See other CYCLIC PEROXIDES

0343. Difluoro-*N*-fluoromethanimine

[338-66-9] **CF_3N**



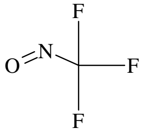
Ginsberg, V. A. *et al., Zh. Obsch. Khim.*, 1967, **37**, 1413

The gas boils at —60°C and explodes in contact with flame.

See other *N*-HALOGEN COMPOUNDS

0344. Nitrosotrifluoromethane

[334-99-6] **CF_3NO**



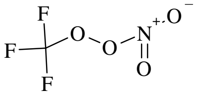
1. Spaziante, P. M., *Intern. Rev. Sci.: Inorg. Chem. Ser. 1*, 1972, **3**, 141
2. Banks, R. E. *et al., J. Chem. Soc., Perkin Trans. 1*, 1974, 2534—2535

Suggestions of untoward hazard inherent in the preparation of nitrosotrifluoromethane by pyrolysis of trifluoroacetyl nitrite [1] are discounted in the later reference, which gives full details of the equipment and procedure that had been used uneventfully during the previous decade [2].

See other NITROSO COMPOUNDS

0345. Trifluoromethyl peroxonitrate

[50311-48-3] **CF_3NO_4**



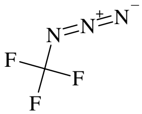
Hohorst, F. A. *et al., Inorg. Chem.*, 1974, **13**, 715

A small sample exploded under a hammer blow.

See other PEROXYESTERS

0346. Trifluoromethyl azide (Azidotrifluoromethane)

[3802-95-7] **CF_3N_3**



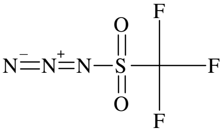
Schack. C. J., *J. Fluorine Chem.*, 1981, **18**, 584

Potentially hazardous, it must be handled with caution.

See other ORGANIC AZIDES

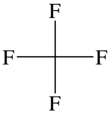
0347. Trifluoromethylsulfonyl azide

[3855-45-6] **$CF_3N_3O_2S$**



Cavender, C. J. *et al., J. Org. Chem.*, 1972, **37**, 3568
An explosion occurred when the azide separated during its preparation in the absence of solvent.
See other ACYL AZIDES

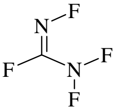
0348. Carbon tetrafluoride (Tetrafluoromethane)
[75-73-0] **CF_4**



Aluminium
See Aluminium: Halocarbons

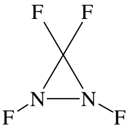
Oxygen, Hydrogen
See other FLUOROCARBONS, HALOALKANES, HALOALKANES

0349. Perfluoroformamidine
[14362-70-0] **CF_4N_2**



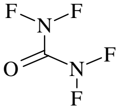
Koshar, R. J. *et al., J. Org. Chem.*, 1967, **32**, 3859, 3862
It explodes on shock or phase change.
See other *N,N,N′*-TRIFLUOROAMIDINES

0350. Tetrafluorodiaziridine
[17224-09-8] **CF_4N_2**



Firth, W. C., *J. Org. Chem.*, 1968, **33**, 3489, 3491
An explosive oxidant, readily initiated by shock or phase changes during condensation or evaporation, especially around —160°C. Handle only small quantities at moderately low temperatures.
See other *N*-HALOGEN COMPOUNDS

0351. Tetrafluorourea
[10256-92-5] **CF_4N_2O**



Acetonitrile

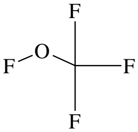
Fraser, G. W. *et al., Chem. Comm.*, 1966, 532

The solution of the difluoroamide in acetonitrile prepared at —40°C must not be kept at ambient temperature, since difluorodiazene is formed.

See Acetonitrile: *N*-Fluoro compounds

See other DIFLUOROAMINO COMPOUNDS

0352. Trifluoromethyl hypofluorite
[373-91-1] **CF_4O**



Hydrocarbons

Allison, J. A. *et al., J. Amer. Chem. Soc.*, 1959, **81**, 1089—1091

In absence of nitrogen as diluent, interaction with acetylene, cyclopropane or ethylene is explosive on mixing, and solutions in benzene explode on sparking or UV irradiation.

See other IRRADIATION DECOMPOSITION INCIDENTS

Hydrogen-containing solvents

1. *Catalogue G-7*, 10, Gainesville (Fa.), Peninsular Chem Research, 1973
2. Barton, D. H. R. *et al., Chem. Comm.*, 1968, 804
3. Robins, M. J. *et al., J. Amer. Chem. Soc.*, 1976, **89**, 7389 (footnote 24)

Contact of the extremely reactive compound with hydrogen-containing solvents or conventional plastics tubing, even at —80°C, is undesirable [1]. Fully halogenated solvents are preferred, and some general precautions are described [2]. Violent explosions have occurred on introducing the gas directly into methanol [3].

Lithium

Porter, R. S. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 5625

Interaction set in at about 170°C with a sufficient exotherm to melt the glass container.

See other GLASS INCIDENTS

Polymers

Barton, D. H. R. *et al., J. Org. Chem.*, 1972, **37**, 329

It is a powerful oxidant and only all-glass apparatus, free of polythene, PVC, rubber or similar elastomers should be used. Appreciable concentrations of the gas in oxidisable materials should be avoided.

Pyridine

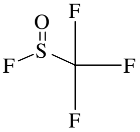
Barton, D. H. R. *et al., Chem. Comm.*, 1968, 804 (footnote)

Use of pyridine as an acid-acceptor in reactions involving trifluoromethyl hypofluorite is discouraged, as a highly explosive by-product is formed.

See other HYPOHALITES, OXIDANTS

0353. Trifluoromethanesulfinyl fluoride

[812-12-4] **CF_4OS**



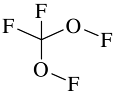
Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

See other ACYL HALIDES

0354. Difluoromethylene dihypofluorite

[16282-67-0] **CF_4O_2**



Haloalkenes

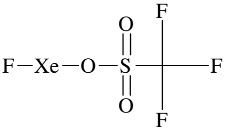
Hohorst, F. A. *et al., Inorg. Chem.*, 1968, **7**, 624

Attempts to react the oxidant with *trans*-dichloroethylene or tetrafluoroethylene at ambient temperature in absence of diluent caused violent explosions. The oxidant should not be allowed to contact organic or easily oxidised material without adequate precautions.

See other HYPOHALITES

0355. Xenon(II) fluoride trifluoromethanesulfonate

[39274-39-0] **CF_4O_3SXe**

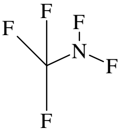


Wechsberg, M. *et al., Inorg. Chem.*, 1972, **11**, 3066

Unless a deficiency of xenon fluoride was used in the preparation at 0°C or below, the title product exploded violently on warming to ambient temperature.

See other XENON COMPOUNDS

0356a. *N,N*-Difluorotrifluoromethylamine (Pentafluoromethanamine)
[335-01-3] **CF_5N**

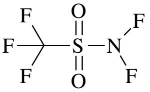


Schack, C. J., *J. Fluorine Chem.*, 1981, **18**, 584

Potentially hazardous, handle with caution.

See other DIFLUOROAMINO COMPOUNDS

0356b. *N,N*,1,1,1-Pentafluoromethanesulfonamide
[54363-74-5] **CF_5NO_2S**

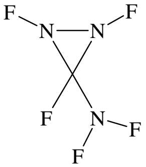


Banks, R. E. *et al., J. Fluor. Chem.*, 2001, **112**(2), 271

This gaseous material is known to be explosive on heating or impact. The monofluorinated amide is also reported as exploding in some circumstances.

See other DIFLUOROAMINO COMPOUNDS

0357. 3-Difluoroamino-1,2,3-trifluorodiaziridine
[17224-08-7] **CF_5N_3**

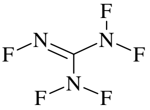


Firth, W. C., *J. Org. Chem.*, 1968, *33*, 3489, 3491

An explosive oxidant, readily initiated by shock or phase change during condensation or evaporation. Only small samples should be used and at moderately low temperatures.

See other DIFLUOROAMINO COMPOUNDS, *N*-HALOGEN COMPOUNDS

0358. Pentafluoroguanidine
[10051-06-6] **CF_5N_3**



Zollinger, J. L. *et al., J. Org. Chem.*, 1973, **38**, 1070—1071

This, and several of its adducts with alcohols, are shatteringly explosive compounds, frequently exploding during phase changes at low temperatures, or on friction or impact.

Liquid fuels

Scurlock, A. C. *et al.*, US Pat. 3 326 732, 1967

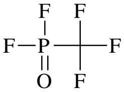
This compound with multiple N—F bonding is useful as an oxidant in propellant technology.

See other DIFLUOROAMINO COMPOUNDS, *N*-HALOGEN COMPOUNDS

See related *N,N,N′*-TRIFLUOROAMIDINES

0359. Difluorotrifluoromethylphosphine oxide

[19162-94-8] **CF_5OP**



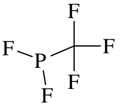
Preparative hazard

See Dinitrogen tetraoxide: Difluorotrifluoromethylphosphine

See related ALKYLHALOPHOSPHINES

0360. Difluorotrifluoromethylphosphine

[1112-04-5] **CF_5P**



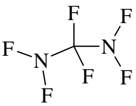
Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Difluorotrifluoromethylphosphine

See other ALKYLHALOPHOSPHINES

0361. Bis(difluoroamino)difluoromethane

[4394-93-8] **CF_6N_2**



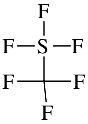
Koshar, R. J. *et al., J. Org. Chem.*, 1966, **31**, 4233

Explosions occurred during the handling of this material, especially during phase transitions. Use of protective equipment is recommended for preparation, handling and storage, even on the microscale.

See other DIFLUOROAMINO COMPOUNDS

0362. Trifluoromethylsulfur trifluoride

[374-10-7] **CF_6S**



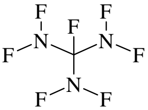
Preparative hazard

See Trifluoromethanesulfenyl chloride: Chlorine fluorides

See other ALKYLNON-METAL HALIDES

0363. Tris(difluoroamino)fluoromethane

[14362-68-6] **CF_7N_3**



Koshar, R. J. *et al., J. Org. Chem.*, 1967, **32**, 3859, 3862

A shock-sensitive explosive, especially in the liquid state (b.p. 5.6°C).

Pentaborane(9)

Marcellis, A. W. *et al.*, US Pat. 4 376 665, 1983

Mixtures prepared at cryogenic temperatures, then allowed to warm, are air-sensitive and powerful explosives.

See other DIFLUOROAMINO COMPOUNDS

0364. Iron carbide

[12011-67-5] **CFe_3**

Fe_3C

Halogens

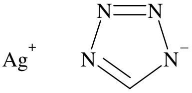
Mellor, 1946, Vol. 5, 898

Incandesces in chlorine below 100°C, and in bromine at that temperature.

See other METAL NON-METALLIDES

0365. Silver tetrazolide

[13086-63-0] **$CHAgN_4$**



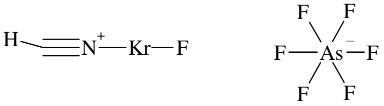
Thiele, J., *Ann.*, 1892, **270**, 59

It explodes on heating.

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS, TETRAZOLES

0366. Fluorohydrocyanokrypton(II) hexafluoroarsenate

[ ] **CHAsF7KrN**



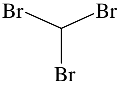
Schrobilgen, G, J., *J. Chem. Soc., Chem. Comm.*, 1988, 863

A white solid precipitating from hydrogen cyanide and fluorokrypton in hydrogen fluoride is attributed this structure. It decomposes rapidly above —50°C, usually with violent detonation.

See other XENON COMPOUNDS

0367. Bromoform (Tribromomethane)

[75-25-2] **$CHBr_3$**



Acetone, Potassium hydroxide

1. Willgerodt, C., *Ber.*, 1881, **14**, 2451
2. Weizmann, C. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 1189

Interaction in presence of powdered potassium hydroxide (or other bases) is violently exothermic [1], even in presence of diluting solvents [2].

See Chloroform: Acetone, etc.

Cyclic poly(ethylene oxides) (‘Crown ethers’), Potassium hydroxide

Le Goaller, R. *et al., Synth. Comm.*, 1982, **12**, 1163—1169

Crown ethers promote dihalocarbene formation from chloroform or bromoform and potassium hydroxide. However, in absence of diluent dichloromethane, dropwise addition of bromoform to the base in cyclohexane led to explosions.

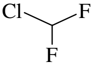
Metals

See Potassium: Halocarbons
Lithium: Halocarbons
METAL—HALOCARBON INCIDENTS

See other HALOALKANES

0368. Chlorodifluoromethane (Freon 22)

[75-45-6] **$CHClF_2$**



HCS 1980, 668 (cylinder)

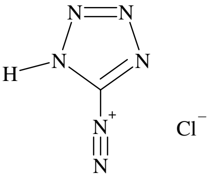
Sand, J. R., *ASHRAE J.*, 1982, **24**(5), 38—40

At elevated pressures, mixtures of the ‘refrigerant 22’ gas with 50% of air are combustible (though ignition is difficult) and a 6—8-fold pressure increase may occur in closed systems if ignition occurs.

Aluminium
See Aluminium: Halocarbons
See other HALOALKANES

0369. Tetrazole-5-diazonium chloride

[27275-90-7] **$CHClN_6$**

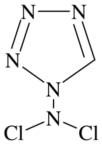


1. Shevlin, P. B. *et al., J. Amer. Chem. Soc.*, 1977, **99**, 2628
2. Klapötke, T. M. *et al., Inorg. Chem.*, 2002, **41**(4), 906

The crystalline diazonium salt will detonate at the touch of a spatula. An ethereal solution exploded violently after 1 h at —78°C, presumably owing to separation of the solid salt [1]. Many explosions were experienced in researches that showed that tetrazolylpentazoles were transient intermediates in reaction of the diazonium salt with lithium azide. There was then decomposition to tetrazolyl azides, themselves very explosive [2].
See 5-Aminotetrazole: Nitrous acid
See other DIAZONIUM SALTS, TETRAZOLES

0370. 1-Dichloroaminotetrazole

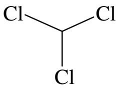
[68594-17-2] **$CHCl_2N_5$**



Karrer, 1950, 804
1-Dichloroaminotetrazole and its 5-derivatives are extremely explosive, as expected in an *N,N*-dichloro derivative of a high-nitrogen nucleus.
See other *N*-HALOGEN COMPOUNDS, TETRAZOLES

0371. Chloroform (Trichloromethane)

[67-66-3] **$CHCl_3$**



(*MCA SD-89*, 1962); *HCS 1980*, 301; *RSC Lab. Hazard Data Sheet No. 44*, 1986

Acetone, Alkali

1. Willgerodt, C., *Ber*, 1881, **14**, 258
2. King, H. K., *Chem. & Ind.*, 1970, 185
3. Hodgson, J. F., *Chem. & Ind.*, 1970, 380
4. Ekely, J. B. *et al., J. Amer. Chem. Soc.*, 1924, **46**, 1253
5. Grew, E. L., *Chem. & Ind.*, 1970, 491
6. Grant, D. H., *Chem. & Ind.*, 1970, 919

Chloroform and acetone interact vigorously and exothermally in presence of solid potassium hydroxide or calcium hydroxide to form 1,1,1-trichloro-2-hydroxy-2-methylpropane [1], and a laboratory incident involving the bursting of a solvent residues bottle was attributed to this reaction. Addition of waste chloroform to a Winchester containing acetone, ether, and petroleum ether chromatography solvent residues led to a vigorous exothermic reaction, the effects of which would be greatly augmented by evolution of vapour of the much lower-boiling solvents in the narrow-necked bottle [2]. No reaction whatsoever occurs in the absence of base, even at 150°C under pressure [1], and the mechanism of the reaction was indicated [3]. Other haloforms and lower ketones react similarly in presence of base [4], but other halocarbons with a less activated hydrogen atom(e.g. dichloromethane) do not undergo the reaction, though there is an exotherm (physical effect) on mixing with acetone [5]. A minor eruption (or sudden boiling) of a chloroform—acetone mixture in new glassware may have been caused by surface alkali [6].

See Bromoform: Acetone, etc.

See other CATALYTIC IMPURITY INCIDENTS, GLASS INCIDENTS

Bis(dimethylamino)dimethylstannane

See Bis(dimethylamino)dimethylstannane: Chloroform

Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Halocarbons

Ethanol (or methanol), Potassium sulfide

See Potassium dithioformate

See Sodium, Methanol; and Sodium methoxide, below

Fluorine

See Fluorine: Halocarbons

Metals MRH Aluminium 3.85/18, magnesium 5.35/23, potassium 4.94/50, sodium 5.81/37

Davis, T. L. *et al., J. Amer. Chem. Soc.*, 1938, **60**, 720—722

The mechanism of the explosive interaction on impact of chloroform with sodium or potassium has been studied.

See other METAL—HALOCARBON INCIDENTS

Nitromethane

See Nitromethane: Haloforms

Other reactants

Yoshida, 1980, 114

MRH values calculated for 14 combinations with a range of materials are given.

Potassium *tert*-butoxide

See Potassium *tert*-butoxide: Acids, etc.

Sodium hydroxide, Methanol

1. *MCA Case History No. 498*
2. *MCA Case History No. 1913*

A chloroform—methanol mixture was put into a drum contaminated with sodium hydroxide. A vigorous reaction set in and the drum burst. Chloroform normally reacts slowly with sodium hydroxide owing to the insolubility of the latter. The presence of methanol (or other solubiliser) increases the rate of reaction by increasing the degree of contact between chloroform and alkali [1]. Addition of chloroform to a 4:1 mixture of methanol and 50 w/v% sodium hydroxide solution caused the drum to burst [2].

Sodium methoxide

1. *MCA Case History No. 693*
2. Kaufmann, W. E. *et al., Org. Synth.*, 1944, Coll. Vol. 1, 258

For the preparation of methyl orthoformate, solid sodium methoxide, methanol and chloroform were mixed together. The mixture boiled violently and then exploded [1]. The analogous preparation of ethyl orthoformate [2] involves the slow addition of sodium or sodium ethoxide solution to a chloroform—ethanol mixture. The explosion was caused by the addition of the solid sodium methoxide as one portion.

See Ethanol (or methanol), Potassium sulfide, above

See Sodium, etc., above

Sodium, Methanol

Unpublished information, 1948

During attempted preparation of trimethyl orthoformate, addition of sodium to an inadequately cooled chloroform—methanol mixture caused a violent explosion.

See Ethanol (or methanol), Potassium sulfide, above

See Sodium methoxide, below

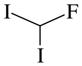
Triisopropylphosphine

See Triisopropylphosphine: Chloroform

See other HALOALKANES

0372. Fluorodiiodomethane

[1493-01-2] **$CHFI_2$**

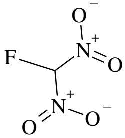


Preparative hazard

See Mercury(I) fluoride: Iodoform

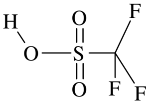
See other HALOALKANES

0373. Fluorodinitromethane
[7182-87-8] **$CHFN_2O_4$**



Potentially explosive.
See entry FLUORODINITROMETHYL COMPOUNDS
See other POLYNITROALKYL COMPOUNDS

0374. Trifluoromethanesulfonic acid ('Triflic acid')
[1493-13-6] **CHF_3O_3S**



Acyl chlorides, Aromatic hydrocarbons

Effenberger, F. *et al., Angew. Chem. (Intern. Ed.)*, 1972, **11**, 300

Addition of catalytic amounts (1%) of the acid (stronger even than perchloric acid) to mixtures of acyl chlorides and aromatic hydrocarbons causes more or less violent evolution of hydrogen chloride, depending on the reactivity of the Friedel-Crafts components.

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

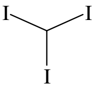
Perchlorate salts

Dixon, N. E. *et al., Inorg. Synth.*, 1986, **24**, 245

Because trifluoromethanesulfonic acid is a stronger acid than perchloric acid, under no circumstances should perchlorate salts be used with the neat acid, because the hot anhydrous perchloric acid so formed represents an extreme explosion hazard, especially in contact with transition metal complexes (or with organic materials).

See Perchloric acid: Dehydrating agents
See other ORGANIC ACIDS

0375. Iodoform (Triiodomethane)
[75-47-8] **CHI_3**



Acetone

See Chloroform: Acetone, etc.

Hexamethylenetetramine

Sorbe, 1968, 137

The 1:1 addition complex exploded at 178°C.

Mercury(I) fluoride

See Mercury(I) fluoride: Iodoform

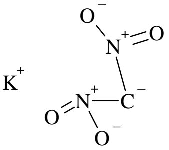
Silver

See Silver: Iodoform

See other ENDOTHERMIC COMPOUNDS, HALOALKANES

0376. Potassium dinitromethanide

[32617-22-4] **$CHKN_2O_4$**



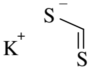
Grakauskas, V. *et al., J. Org. Chem.*, 1978, **43**, 3486

Alkali-metal salts of of dinitromethane are sensitive to impact and should be handled remotely behind shields, in small quantity and with great care.

See other POLYNITROALKYL COMPOUNDS

0377. Potassium dithioformate

[30962-16-4] **$CHKS_2$**



Preparative hazard

1. Martin, K., *Chem. Brit.*, 1988, **24**, 427—428
2. Engler, K., *Z. Allgem. Anorg. Chem.*, 1972, **389**, 145
3. Yoshida, 1980, 387

Potassium dithioformate is prepared by interaction of chloroform with potassium sulfide in ethanol, via a carbene reaction, possibly involving the 3 main stages

$CHCl_3 + K_2S \rightarrow :CCl_2 + KSH + KCl$

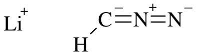
$:CCl_2 + KSH \rightarrow KSCHCl_2$

$KSCHCl_2 + K_2S \rightarrow KSC(S)H + 2KCl$

The reaction has been found unpredictable in practice, 2 out of 3 attempts leading to eruption or explosion of the flask contents [1]. However, using a modified version of a published procedure [2], with methanol as solvent, the reaction can be performed without incident, provided that the working scale is restricted to one third of that published (and initially one twelfth until one gains experience of the reaction); that a flanged reaction flask is used; and that the rate of addition of chloroform to the methanolic potassium sulfide is carefully controlled to 4—5 drops/s. This is essential, for if too slow the reaction stops, and if too fast it becomes uncontrollable [1]. Though no figures for the more reactive chloroform are given, the MRH value for a mixture of potassium sulfide with 41 wt% of carbon tetrachloride is 2.05 kJ/g [3].

0378. Lithium diazomethanide

[67880-27-7] **$CHLiN_2$**



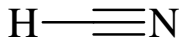
Müller, E. *et al., Chem. Ber.*, 1954, **87**, 1887

Alkali metal salts of diazomethane are very explosive when exposed to air in the dry state, and should be handled, preferably wet with solvent, under an inert atmosphere.

See other DIAZO COMPOUNDS

†0379a. Hydrogen cyanide

[74-90-8] **CHN**



(*MCA SD-67*, 1961); *FPA H94*, 1980; *HCS 1980*, 547 (neat), 542 (solutions)

1. *MCA SD-67*, 1961
2. Wöhler, L. *et al., Chem. Ztg.*, 1926, **50**, 761, 781
3. Gause, E. H. *et al., J. Chem. Eng. Data*, 1960, **5**, 351
4. Salomone, G., *Gazz. Chim. Ital. [I]*, 1912, **42**, 617—622
5. Anon., *Jahresber.*, 1979, 70—71
6. Bond, J., *Loss Prev. Bull.*, 1991, **101**, 3

Hydrogen cyanide is highly endothermic and of low MW (ΔH_f°(g) +130.5 kJ/mol, 4.83 kJ/g). A comprehensive guide to all aspects of industrial handling of anhydrous hydrogen cyanide and its aqueous solutions states that the anhydrous liquid is stable at or below room temperature if it is inhibited with acid (e.g. 0.1% sulphuric acid) [1]. Presence of alkali favours explosive polymerisation [2]. In absence of inhibitor, exothermic polymerisation occurs, and if the temperature attains 184°C, explosively rapid polymerisation occurs [3]. A 100 g sample of 95—96% material stored in a glass bottle shielded from sunlight exploded after 8 weeks [4]. The explosive polymerisation of a 33 kg cylinder was attributed to lack of sufficient phosphoric acid as stabiliser [5]. A tank containing 4 or 5 tonnes of hydrogen cyanide exploded with the force of several kg of TNT, leading to an HCN fire. This was easily extinguished, the clear-up thereafter being impeded by the toxicity of the unburnt cyanide. The explosion was attributed to build up of polymer (the reaction is autocatalytic because of ammonia generation), insufficient stabiliser (oxalic acid), lower than usual purity (<93%) and possibly to mercury contamination. It was recommended that HCN should not be stored if overwet,

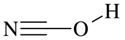
that tanks should be regularly emptied to inspect for polymer, and that stabiliser should be added before running to storage [6].
See Mercury(II) cyanide: Hydrogen cyanide
See other GLASS INCIDENTS, POLYMERISATION INCIDENTS

Alcohols, Hydrogen chloride
See Hydrogen chloride: Alcohols, etc.

Hypochlorites
See CYANIDES

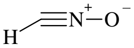
Other reactants
Yoshida, 1980, 136
MRH values for 15 combinations, mainly with oxidants, are given
See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, ORGANIC ACIDS

0379b. Cyanic acid (Isocyanic acid)
[420-05-3] [75-13-8] iso- CHNO



Rodd, 2nd Edn., Vol. Ic, 354, 1965
The anhydrous acid is obtainable by pyrolysis of the trimer, to which it may revert violently above 0°C. Only one acid is obtainable from both cyanates and isocyanates.

0380. Fulminic acid (Hydrogen cyanide *N*-oxide)
[506-85-4] CHNO

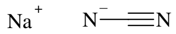


1. Sorbe, 1968, 72
2. Wentrup, C. *et al., Angew. Chem. (Intern. Ed.)*, 1979, **18**, 467

It is fairly stable as an ethereal solution, but the isolated acid is explosively unstable, and sensitive to heat, shock or friction [1]. In a new method of preparation of the acid or its salts, pyrolysis of 4-oximato-3-substituted-isoxazol-5(4*H*)-ones or their metal salts must be conducted with extreme care under high vacuum to prevent explosive decomposition [2].
See METAL FULMINATES
Silver 3-methylisoxazolin-4,5-dione-4-oximate
Sodium 3-methylisoxazolin-4,5-dione-4-oximate
Sodium 3-phenylisoxazolin-4,5-dione-4-oximate
See other *N*-OXIDES

0381. Monosodium cyanamide

[17292-62-5] CHN$_2$Na



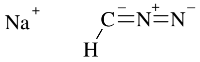
tert-Butyl hypochlorite

See Cyanonitrene

See other CYANO COMPOUNDS, *N*-METAL DERIVATIVES

0382. Sodium diazomethanide

[67880-28-8] CHN$_2$Na

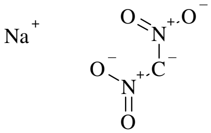


See Lithium diazomethanide

See other DIAZO COMPOUNDS

0383. Sodium dinitromethanide

[25854-41-5] CHN$_2$NaO$_4$



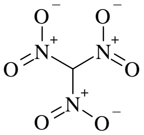
Grakauskas, V. *et al., J. Org. Chem.*, 1978, **43**, 3486

Alkali-metal salts of dinitromethane are sensitive to impact and should be handled remotely behind shields in small quantity, and with great care.

See other POLYNITROALKYL COMPOUNDS

0384. Trinitromethane ('Nitroform')

[517-25-9] CHN$_3$O$_6$



1. Marans, N. S. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 5329
2. Stull, 1977, 20

Explosions occurred during distillation of this polynitro compound [1]. Though not an endothermic compound, it is of positive oxygen balance and the heat of decomposition (2.80 kJ/g) would give an adiabatic decomposition temperature exceeding 2200°C and a 40-fold increase in pressure [2].

See entry OXYGEN BALANCE

Divinyl ketone

Graff, M. *et al., J. Org. Chem.*, 1968, **33**, 1247

One attempted reaction of trinitromethane with impure ketone caused an explosion at refrigerator temperature.

2-Propanol

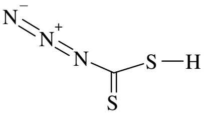
MCA Case History No. 1010

Frozen mixtures of trinitromethane—2-propanol (9:1) exploded during thawing. The former (of positive oxygen balance) dissolves exothermally in the alcohol, the heat effect increasing directly with the concentration above 50% w/w. Traces of nitric acid may also have been present.

See other POLYNITROALKYL COMPOUNDS

0385a. Azidodithioformic acid (Azidodithiocarbonic acid)

[4472-06-4] **CHN_3S_2**



1. Mellor, 1947, Vol.8, 338
2. Smith, G. B. L., *Inorg. Synth.*, 1939, **1**, 81
3. Klapötke, T. M., *et al., Inorg. Chem.*, 2004, **43**(4), 1370

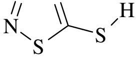
The isolated acid or its salts are shock- and heat-sensitive explosives [1]. Safe preparative procedures have been detailed [2]. Anhydrous salts should be handled only in small quantities and shielded from electrostatic discharge. Although names reflecting the preparation from azide are still in use (2005) the actual structure of the salts and disulfide derives from the cyclic 1,2,3,4-thiatriazole-5-thiol, and the tautomeric thiatriazolidinethione forms the isolable free 'acid' [3]. The heavy metal salts, though powerful detonators, are too sensitive for practical use [2].

See Bis(azidothiocarbonyl) disulfide

See Carbon disulfide: Metal azides

See other ACYL AZIDES, ORGANIC ACIDS

0385b. 1,2,3,4-Thiatriazole-5-thiol **CHN_3S_2**



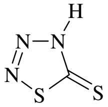
Klapötke, T. M., *et al., Inorg. Chem.*, 2004, **43**(4), 1370

The structure of the parent acid of salts obtainable from reaction of azides and carbon disulfide and still often called azidodithio-formates or -carbonates.The isolable 'acid' has an isomeric thione structure.

See Azidodithioformic acid

0385c. 2-*H*-1,2,3,4-Thiatriazolidine-5-thione

[52098-76-7] **CHN_3S_2**



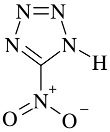
Klapötke, T. M., *et al., Inorg. Chem.*, 2004, **43**(4), 1370

The true structure of isolated azidodithioformic acid.

See Azidodithioformic acid

0386a. 5-Nitrotetrazole

[55011-46-6] **CHN_5O_2**



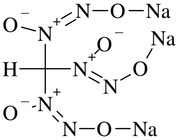
1. Jenkins, J. M., *Chem. Brit.*, 1970, **6**, 401
2. Bates, L. R. *et al.*, US Pat. 4 094 879, 1978
3. Koldobskii, G. I. *et al., Russ. J. Org. Chem.*, 1997, **33**(12), 1771

An acidified solution of the sodium salt was allowed to evaporate during 3 days and spontaneously exploded 2 weeks later. The nature of the explosive species, possibly the *aci*-tetrazolic acid, was being sought [1]. The silver and mercury salts are explosive [2]. The chemical properties of the free nitrotetrazole have been studied. The sodium salt tetrahydrate loses water above 50°C, greatly increasing its friction and shock sensitivity [3].

See other C-NITRO COMPOUNDS, TETRAZOLES

0386b. Sodium methanetris(diazeniumdiolate)

[381228-05-3] [381228-06-4] hydrate [418760-19-7] trihydrate **$CHN_6Na_3O_6$**



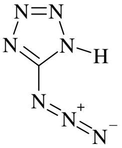
Arnold, E. V. *et al., Chem. Lett.*, 2002, **4**(8) 1323

This compound may result when other nucleophilic materials are treated with nitric oxide in acetonitrile solvent, common reaction conditions for diazeniumdiolate preparation. Poly(diazeniumdiolates)can be violently unstable and need handling with care.

See other N—O COMPOUNDS

0387. 5-Azidotetrazole

[35038-46-1] **CHN_7**



Alone, or Acetic acid, or Alkali

1. Thiele, J. *et al., Ann.*, 1895, **287**, 238
2. Lieber, E. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 1313

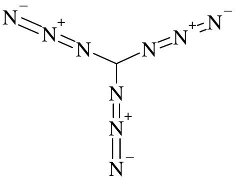
Though explosive, it (and its ammonium salt) are much less sensitive to impact or friction than its sodium or potassium salts [1]. A small sample of the latter exploded violently during vacuum filtration. The parent compound explodes spontaneously even in acetone (but not in ethanol or aqueous) solution if traces of acetic acid are present [2]. The salts are readily formed from diaminoguanidine salts and alkali nitrites. The ammonium salt explodes on heating, and the silver salt is violently explosive even when wet [1]. The sodium salt is also readily formed from cyanogen azide.

See Sodium 5-azidotetrazolide

See other ORGANIC AZIDES, TETRAZOLES

0388. Triazidomethane

[107585-04-6] **CHN_9**



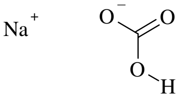
1. Hassner, A., private comm., 1986
2. Hassner, A. *et al., J. Org. Chem.,* 1990, **55**, 2304

The azide form of the quaternary ammonium ion exchange resin IR-400 (which exhibits low friction-sensitivity) reacts with bromoform, analogously to dichloro- and dibromomethane, to form the highly explosive triazidomethane. Solutions of above 50% concentration explode in contact with a pipette or on injection into a GLC inlet port.

See other ORGANIC AZIDES

0389. Sodium hydrogen carbonate

[144-55-8] **$CHNaO_3$**



HCS 1980, 828

Carbon, Water

CISHC Chem. Safety Summ., 1978, **49**, 33

A mixture was being stirred and steam heated when power failure interrupted stirring, and heating was turned off for a hour before power was restored. When stirring was restarted, the hot contents of the pan erupted immediately. Carbon dioxide is evolved from warm aqueous solutions of the base, and absence of stirring and presence of the carbon adsorbent would lead to non-equilibrium retention of the gas, which would be released instantaneously on stirring.

See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS

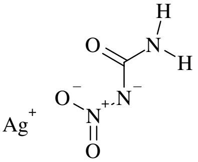
2-Furaldehyde

See 2-Furaldehyde

See other INORGANIC BASES, METAL OXONON-METALLATES

0390. Silver nitroureide

[74386-96-2] (ion) **$CH_2AgN_3O_3$**

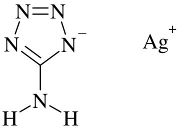


See Nitrourea

See other *N*-METAL DERIVATIVES, N—NITRO COMPOUNDS, SILVER COMPOUNDS

0391. Silver 5-aminotetrazolide

[50577-64-5] (ion) **CH_2AgN_5**



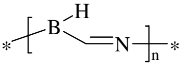
Thiele, J., *Ann.*, 1892, **270**, 59

Similar to silver tetrazolide, it explodes on heating.

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS, TETRAZOLES

0392. Cyanoborane oligomer

[60633-76-3] **$(CH_2BN)_n$**



Gyori, B. *et al., J. Organomet. Chem.*, 1984, **262**, C7

It explodes on mechanical shock, and decomposes violently on heating under nitrogen to 230°C. The scale of preparation may need to be limited.

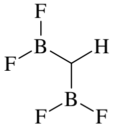
Sodium chlorate

See Sodium chlorate: Cyanoborane oligomer

See related BORANES, CYANO COMPOUNDS

0393. Bis(difluoroboryl)methane

[55124-14-6] **$CH_2B_2F_4$**



Air, or Water

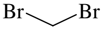
Maraschin, N. J. *et al., Inorg. Chem.*, 1975, **14**, 1856

Highly reactive, it explodes on exposure to air or water.

See related ALKYLHALOBORANES

0394. Dibromomethane

[74-95-3] **CH_2Br_2**



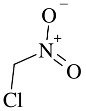
Potassium

See Potassium: Halocarbons

See other HALOALKANES

0395. Chloronitromethane

[1794-84-9] **CH_2ClNO_2**



Preparative hazard

1. Seigle, L. W. *et al., J. Org. Chem.*, 1940, **5**, 100
2. Libman, D. D., private comm., 1968

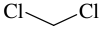
Chlorination of nitromethane following the published general method [1] gave a product which decomposed explosively during distillation at 95 mbar [2]. A b.p. of 122°C/1 bar is quoted in the literature.

See Sodium *aci*-nitromethanide: Carbon disulfide, Chlorine

See related NITROALKANES

†0396. Dichloromethane

[75-09-2] **CH_2Cl_2**



(*MCA SD-86*, 1962); *NSC 474*, 1979; *HCS 1980*, 648

1. *RSC Lab. Hazard Data Sheet No. 3*, 1982
2. Downey, J. R., *Chem. Eng. News*, 1983, **61**(8), 2
3. Kelling, R. A., *Chem. Eng. News*, 1990, **68**(17), 2
4. Kong, D. *et al., J. Haz. Mat.*, 2003, **102**(2-3), 155

Previously thought to be non-flammable except at elevated temperature or pressure or in oxygen-enriched air [1], it is in fact flammable in the range 12—19% in ambient air, given a sufficiently high level of ignition energy. Though it has no measurable flash point, it is calculated that flammable regions may exist above —9°C [2]. In oxygen the flashpoint is −7°C [4]. A surprisingly violent burst of a half full separating funnel occurred when dichloromethane was shaken with water, air also being present [3].

See FLASH POINTS (reference 19)

Air, Methanol

Coffee, R. D. *et al., J. Chem. Eng. Data*, 1972, **17**, 89—93

Dichloromethane, previously considered to be non-flammable except in oxygen, becomes flammable in air at 102°C/1 bar, at 27°C/1.7 bar or at 27°C/1 bar in presence of less than 0.5 vol% of methanol (but see reference 2 above). Other data are also given.

Aluminium

See Aluminium: Dichloromethane

See Metals, below

Aluminium bromide

See Aluminium bromide: Dichloromethane

Azides

See Quaternary ammonium azides, below; Sodium azide, below

1,2-Diaminoethane

1. Nolan, 1983, Case history 145
2. Heskey, W. A., *Chem. Eng. News*, 1986, **64**(21), 2
3. Laird, T., *Chem. & Ind.*, 1986, 139

Dichloromethane was being distilled from its mixture with the amine at a bath temperature of 30°C when an exothermic reaction led to deflagration [1]. Heat of reaction, ΔH = —343 kJ/mol (4.04 kJ/g) of dichloromethane [2]. Reaction of amines with dichloromethane at ambient temperature is common, exothermic in conc. solutions, and involves formation of an *N*-chloromethyl quaternary salt. Concentrating dichloromethane solutions of amines to low volumes should therefore be avoided [3].

Dimethyl sulfoxide, Perchloric acid
See Perchloric acid: Dichloromethane, Dimethyl sulfoxide

Dinitrogen pentaoxide
See NITRATING AGENTS

Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Halocarbons

Metals
See Aluminium: Halocarbons
Lithium: Halocarbons
METAL—HALOCARBON INCIDENTS
Sodium: Halocarbons

Nitric acid
See Nitric acid: Dichloromethane

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

Quaternary ammonium azides

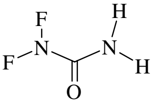
1. Hassner, A. *et al., Angew. Chem. (Intern. Edn.)*, 1986, **25**, 479—480
2. Demer, F. R., *Lab. Safety Notes* (Univ. of Arizona), 1991(Spring), 2
3. Wood, W., private comm., 1986
4. Bretherick, L., *Chem. Eng. News*, 1986, **64**(51), 2
5. Editor's comments, 2001

Quaternary ammonium azides will displace halogens in a synthesis of alkyl azides. Dichloromethane has been used as a solvent, although this can slowly form diazidomethane which may be concentrated by distillation during work-up, thereafter easily exploding [1]. An accident attributed to this cause is described, and acetonitrile recommended as a preferable solvent, supported polymeric azides, excess of which can be removed by filtration are also preferred in place of the tetrabutylammonium salt [2]. It should be noted that the substrate in this case, a 3-phenyl-2-bromopropionamide, might fairly readily eliminate hydrogen bromide and that it was the cold traps on a rotary evaporator which accumulated the explosive. This makes hydrogen azide generation and concentration a plausible alternative explanation [5]. A similar explosion was previously recorded when the quaternary azide was generated in situ from sodium azide and a phase transfer catalyst in a part aqueous system [3,4].

Sodium azide
See Quaternary ammonium azides, above
See other HALOALKANES

0397a. 1,1-Difluorourea

[1510-31-2] **$CH_2F_2N_2O$**



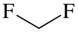
Parker, C. O. *et al., Inorg. Synth.*, 1970, **12**, 309

Concentrated aqueous solutions of difluorourea decompose above —20°C with evolution of tetrafluorohydrazine and difluoramine, both explosive gases.

See other DIFLUOROAMINO COMPOUNDS, GAS EVOLUTION INCIDENTS

†0397b. Difluoromethane

[75-10-5] **CH_2F_2**

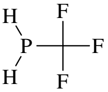


1. Womeldorf, C., *et al., Combust. Flame*, 1999, **118**(1/2), 25
2. Losochkin, Ya. A. *et al., Chem. Abs.*, 2002, **136**, 155453a

Like dichloromethane, the fluoro- analogue is weakly flammable, with flammability not revealed by many conventional tests. A new method of measurement is described [1]. The explosion properties with air of both difluoro- and chlorofluoro-methane have been studied [2].

0398. Trifluoromethylphosphine

[420-52-0] **CH_2F_3P**



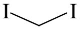
491M, 1975, 428

Ignites in air.

See other ALKYLPHOSPHINES

0399. Diiodomethane

[75-11-6] **CH_2I_2**



Moderately endothermic: ΔH_f° 69 kJ/mole. Expressed as kJ/g this is trivial, 0.26 kJ/g, but the rules of thumb relating energy per g to explosivity are based on complex organic molecules with the ability to disperse energy into numerous vibrational modes. Heavy atoms have not such possibilities.

See other ENDOTHERMIC COMPOUNDS

Alkenes, Diethylzinc

See Diethylzinc: Alkenes, Diiodomethane

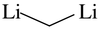
Metals

See Copper—zinc alloys: Diiodomethane, etc.
Lithium: Halocarbons
METAL—HALOCARBON INCIDENTS
Potassium: Halocarbons

See other ENDOTHERMIC COMPOUNDS, HALOALKANES

0400. Methylenedilithium

[21473-62-1] **CH_2Li_2**

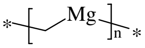


491M, 1975, 234

Ignites in air.
See other ALKYLMETALS

0401. Methylenemagnesium

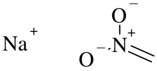
[25382-52-9] **CH_2Mg**



Ziegler, K. *et al., Z. Anorg. Chem.*, 1955, **282**, 345
The polymeric form ignites in air.
See other ALKYLMETALS

0402. Sodium *aci*-nitromethanide

[25854-38-0] **CH_2NNaO_2**



Meyer, V., *et al., Ber.*, 1894, **27**, 1601; 3407
Sodium nitromethanoate is relatively stable when solvated. The dry salt is a sensitive and powerful explosive which may be detonated by warming to 100°C, by a strong blow or contact with traces of water. The potassium salt is even more sensitive. Lecture demonstrations of these properties are described.
See Nitromethane: Sodium hydride

Carbon disulfide, Chlorine

1. Stirling, C. J. M., *Chem. Brit.*, 1986, **22**, 524
2. Stirling, C. J. M., private comm., 1986

During the preparation of chloronitromethane by adding portions of dry sodium *aci*-nitromethanide to chlorine (40 mol of each) dissolved in carbon disulfide, a violent explosion occurred when the addition was half-complete. Similar reactions using bromine had been executed uneventfully many times previously [1]. No certain explanation has emerged, but the sodium salt is known to be explosively unstable, and mixtures of carbon disulfide vapour and air are of course extremely flammable and explosive. Contact of the dry salt with traces of chlorine above its carbon disulfide solution may have led to an exotherm and ignition of the vapour—air mixture in the flask [2].

Mercury(II) chloride, Acids

Nef, J. U., *Ann.*, 1894, **280**, 263, 305

Interaction gives mercury nitromethanide, which is converted by acids to mercury fulminate.

See Mercury(II) fulminate

Nitric oxide, Base

Traube, W., *Annalen*, 1898, **300**, 107

A slurry of sodium nitromethanoate in excess sodium ethoxide solution forms a (presumably even more) explosive salt on treatment with nitric oxide. It is claimed the parent acid is $O_2NCH_2N_2O_2H$.

See Nitrogen oxide

1,1,3,3-Tetramethyl-2,4-cyclobutanedione

See Sodium 1,3-dihydroxy-1,3-bis(*aci*-nitromethyl)-2,2,4,4-tetramethylcyclobutandiide

Water

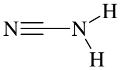
1. Nef, J. U., *Ann.*, 1894, **280**, 273
2. Jung. M. E. *et al., J. Chem. Soc., Chem. Comm.*, 1987, 753 (footnote)

The *aci*-sodium salt, normally crystallising with one molecule of ethanol and stable, will explode if moistened with water. This is due to liberation of heat and conversion to sodium fulminate [1]. After several uneventful similar operations, during the destruction of excess sodium salt by pouring water onto it, a violent explosion occurred [2]. A safer procedure would be to add the salt in small portions to a bulk of stirred ice-water.

See also Sodium 1,3-dihydroxy-1,3-bis(*aci*-nitromethyl)-2,2,4,4-tetramethylcyclobutandiide, *aci*-nitro salts

0403. Cyanamide

[420-04-2] **CH_2N_2**



1. Anon., *Fire Prot. Assoc. J.*, 1966, 243
2. Anon., *Sichere Chemiearbeit*, 1976, **28**, 63

Cyanamide is endothermic (ΔH_f° +58.8 kJ/mol, 1.40 kJ/g), thermally unstable and needs storage under controlled conditions. Contact with moisture, acids or alkalies accelerates the rate of decomposition, and at temperatures above 40°C thermal decomposition is rapid and may become violent. A maximum storage temperature of 27°C is recommended [1]. Commercial cyanamide is stabilised with boric acid, phosphoric acid, sodium dihydrogen phosphate etc., but vacuum distillation produces a neutral (unstabilised) distillate, which immediately may decompose spontaneously. Small-scale storage tests showed that unstabilised cyanamide was 47% decomposed after 18 days at 20°C and 75% decomposed after 29 days at 30°C, whereas stabilised material showed only 1% decomposition under each of these conditions. Larger-scale tests with 1—2 kg unstabilised samples led to sudden and violent exothermic polymerisation after storage for 14 days at ambient temperature. If small samples of unstabilised cyanamide are required, they are best prepared by freezing out from aqueous solutions of the stabilised material. Such small samples should be used immediately or stored under refrigeration [2].

1,2-Phenylenediamine salts

Sawatari, K. *et al.*, Japan Kokai, 76 16 669, 1976 (*Chem. Abs.*, 1976, **85**, 63069)

During the preparation of 2-aminobenzimidazoles, reaction conditions are maintained below 90°C to prevent explosive polymerisation of cyanamide.

Water

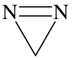
Pinck, L. A. *et al., Inorg. Synth.*, 1950, **3**, 41

Evaporation of aqueous solutions to dryness is hazardous, owing to the possibility of explosive polymerisation in conc. solution.

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, POLYMERISATION INCIDENTS

0404. Diazirine

[157-22-2] **CH_2N_2**



1. Graham, W. H., *J. Org. Chem.*, 1965, **30**, 2108
2. Schmitz, E. *et al., Chem. Ber.*, 1962, **95**, 800

This cyclic isomer of diazomethane is also a gas (b.p., —14°C) which explodes on heating. Several homologues are also thermally unstable [1][2].

See other DIAZIRINES

0405. Diazomethane

[334-88-3] **CH_2N_2**

$$=\overset{+}{N}=N^{-}$$

RSC Lab. Hazard Data Sheet No. 4, 1982

1. Eistert, B., in *Newer Methods of Preparative Organic Chemistry*, 517—518, New York, Interscience, 1948
2. de Boer, H. J. *et al., Org. Synth.*, 1963, Coll. Vol. 4, 250
3. Gutsche, C. D., *Org. React.*, 1954, **8**, 392—393
4. Zollinger, H., *Azo and Diazo Chemistry*, 22, London, Interscience, 1961

5. Fieser, L. *et al., Reagents for Organic Synthesis*, Vol. 1, 191, New York, Wiley, 1967
6. Horàk, V. *et al., Chem. & Ind.*, 1961, 472
7. Ruehle, P. H. *et al., Chem. & Ind.*, 1979, 255—256
8. Bowes, C. M., *Univ. Safety Assoc. Safety News*, 1981, **15**, 18—19
9. Hashimoto, N. *et al., Chem. Pharm. Bull.*, 1981, **29**, 1475—1478; 1982, **30**, 119—124
10. Barnes, C. J. *et al., J. Assoc. Off. Anal. Chem.*, 1982, **65**, 273—274
11. Black, H. T., *Aldrichimica Acta*, 1983, **16**(1), 3—10
12. Asyama, T. *et al., Chem. Abs.*, 1984, **101**, 171306
13. Shiga, S., *Chem. Abs.*, 1987, **107**, 117404
14. Carlton, L. *et al., S. African J. Chem.*, 1987, **40**, 203—204
15. Archibald, T. G. *et al.*, US Patent 5,817,778, 1998

Diazomethane is a highly endothermic small molecule (ΔH_f° (g) +192.5 kJ/mol, 4.58 kJ/g) which boils at —23°C and the undiluted liquid or concentrated solutions may explode if impurities or solids are present [1], including freshly crystallised products [2]. Gaseous diazomethane, even when diluted with nitrogen, may explode at elevated temperatures (100°C or above), or under high-intensity lighting, or if rough surfaces are present [1]. Ground glass apparatus or glass-sleeved stirrers are therefore undesirable when working with diazomethane. Explosive intermediates may also be formed during its use as a reagent, but cold dilute solutions have frequently been used uneventfully [1]. Further safety precautions have been detailed [2,3,4]. Many precursors for diazomethane generation are available [5], including the stable water soluble intermediate *N*-nitroso-3-methylaminosulfolane [6]. Many of the explosions observed are attributed to uncontrolled or unsuitable conditions of contact between concentrated alkali and undiluted nitroso precursors [1].

A large scale generator and procedure for safe preparation and use of the reagent on 1.1 mol scale are detailed [7]. Insolubility of the substrate in ether led to omission of ether from a microgenerator chamber and use of dioxan to dissolve the substrate in the outer chamber. During addition of alkali to nitrosomethylguanidine (30 mg) in 0.125 ml water, the apparatus exploded. This was attributed to absence of ether vapour to dilute the diazomethane [8]. Trimethylsilyldiazomethane is presented as a safe and effective substitute for the hazardous parent compound [9], and two cheap and safe storage containers for small amounts of ethereal solutions of the latter are described [10]. The available data has been summarised with 116 references [11]. The preparation of trimethylsilyldiazomethane and its application as a safe substitute for diazomethane are reviewed [12]. Automated equipment for esterification of small samples of acidic materials for GLC analysis has been developed [13]. A convenient method for preparation of small amounts of pure diazomethane involves entrainment in a stream of helium and condensation as a solid, m.p. —145°C, on a liquid nitrogen-cooled cold finger. The solid may be kept almost indefinitely at LN temperature [14]. Procedures for small industrial scale (50 mole) preparation and use in solution have been patented [15].

See also GLASS INCIDENTS

Alkali metals

Eistert, B. in *Newer Methods of Preparative Organic Chemistry*, 518, New York, Interscience, 1948

Contact of diazomethane with alkali metals causes explosions.

See Lithium diazomethanide

Calcium sulfate

Gutsche, C. D., *Org. React.*, 1954, **8**, 392

Calcium sulfate is an unsuitable desiccant for drying tubes in diazomethane systems. Contact of diazomethane vapour and the sulfate causes an exotherm which may lead to detonation. Potassium hydroxide is a suitable desiccant.

Dimethylaminodimethylarsine, Trimethyltin chloride

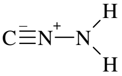
Krommes, P. *et al., J. Organomet. Chem.*, 1976, **110**, 195—200

Interaction in ether to produce diazomethyldimethylarsine is accompanied by violent foaming, and eye protection is essential.

See other DIAZO COMPOUNDS, ENDOTHERMIC COMPOUNDS

0406. Isocyanoamide (‘Isodiazomethane’)

[4702-38-9] **CH_2N_2**



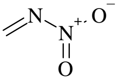
1. Müller, E. *et al., Chem. Ber.*, 1954, **87**, 1887
2. Müller, E. *et al., Ann.*, 1968, **713**, 87

This unstable liquid begins to decompose at 15°C and explodes exothermically at 35—40°C [1], but may be handled safely in ether solution [2].

See related CYANO COMPOUNDS

0407. *N*-Nitromethanimine

[64700-85-2] **$CH_2N_2O_2$**



Zhao, X. *et al., J. Chem. Phys.*, 1988, **88**, 801

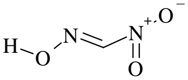
This nitrimine, the nominal monomer of the cyclic nitramine high explosives RDX and HMX, may be involved in their detonation and can be formed from them by pyrolysis.

See 1,3,5-Trinitrohexahydro-1,3,5-triazine

See other N—NITRO COMPOUNDS

0408. Nitrooximinomethane (‘Methylnitrolic acid’)

[625-49-0] **$CH_2N_2O_3$**



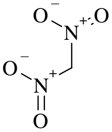
Sorbe, 1968, 147

An unstable and explosive crystalline solid, formally a nitro-oxime.

See related NITROALKANES, OXIMES

0409. Dinitromethane

[625-76-3] **$CH_2N_2O_4$**



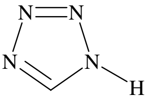
1. Sorbe, 1968, 148
2. Bedford, C. D. *et al., J. Org. Chem.*, 1979, **44**, 635

It explodes at 100°C [1], and attempted distillation of more than 1 g at 30—35°C/1.5 mbar led to a violent explosion [2].

See other POLYNITROALKYL COMPOUNDS

0410a. Tetrazole

[288-94-8] **CH_2N_4**



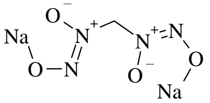
1. Benson, F. R., *Chem. Rev.*, 1947, **41**, 5
2. Stull, 1977, 22
3. *DOC 5*, 1982, 5032
4. Anon., *IST Sci. Tech.*, 1987, (4), 9

It explodes above its m.p., 155°C [1]. It is highly endothermic (ΔH_f° +237.2 kJ/mol, 3.39 kJ/g) with a heat of decomposition (3.27 kJ/g) which would give an adiabatic product temperature of some 1950°C and a 22-fold increase in pressure in a closed container [2]. Its solutions are also explosive when shocked [3]. An explosion during sublimation of tetrazole at ambient pressure was caused by overheating [4].

See other ENDOTHERMIC COMPOUNDS, TETRAZOLES

0410b. Disodium methanebis(diazene-*N*-oxide-*N′*-hydroxylate) [62502-73-2] [381228-07-5] hydrate

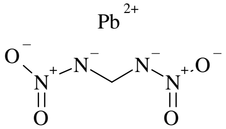
$CH_2N_4Na_2O_4$



See Nitrogen oxide: Acetone, base

0411. Lead methylenebis(nitramide) (*N,N′*-Dinitromethanediamine, lead(II) salt) [86202-43-9]

$CH_2N_4O_4Pb$

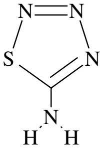


See Methylenebis(nitramine)

See other HEAVY METAL DERIVATIVES, N—NITRO COMPOUNDS

0412. 5-Amino-1,2,3,4-thiatriazole [6630-99-5]

CH_2N_4S



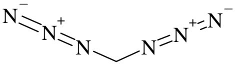
Lieber, E. *et al., Inorg. Synth.*, 1960, **6**, 44

It decomposes with a slight explosion in a capillary tube at 136°C.

See other HIGH-NITROGEN COMPOUNDS, N—S COMPOUNDS

0413. Diazidomethane [107585-03-5]

CH_2N_6



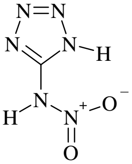
1. Hassner, A. *et al., Angew. Chem. (Intern. Ed.)*, 1986, **25**, 479—480
2. Hassner, A. *et al., J. Org. Chem.*, 1990, **55**, 2304

The azide form of the quaternary ammonium ion exchange resin IR-400 (which exhibits low friction-sensitivity) reacts very slowly with dichloromethane or dibromomethane to produce the explosive diazidomethane [1]. Solutions of above 70% concentration will explode if a pipette is inserted or on injection into a GLC inlet port [2].

See other ORGANIC AZIDES

0414. 5-*N*-Nitroaminotetrazole

[18588-16-4] **$CH_2N_6O_2$**



1. Lieber, E. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 2328
2. O'Connor, T. E. *et al., J. Soc. Chem. Ind.*, 1949, **68**, 309

It and its monopotassium salt explode at 140°C and the diammonium salt explodes at 220°C after melting [1]. The disodium salt explodes at 207°C [2].

Amminemetals

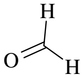
Complexes with several ammine derivatives of metals are explosive.

See entry NITRAMINE—METAL COMPLEXES

See other *N*-NITRO COMPOUNDS, TETRAZOLES

†0415. Formaldehyde

[50-00-0] **CH_2O**



(*MCA SD-1*, 1960); *NSC 342*, 1982; *FPA H54*, 1977; *HCS 1980*, 506

van den Brink, M. J., *Chem. Mag.* (Rijswijk), 1982, 428

Pure formaldehyde, prepared by vacuum depolymerisation of paraldehyde, was collected as a solid at —189°C. When the flask was transferred to a Cardice—ethanol bath, the contents began to repolymerise exothermally and ignited.

See Glyoxal

See other POLYMERISATION INCIDENTS

Acrylonitrile

See Acrylonitrile, Formaldehyde

Hydrogen peroxide MRH 6.44/69

See Hydrogen peroxide: Oxygenated compounds

Magnesium carbonate hydroxide

BCISC Quart. Safety Summ., 1965, **36**(143), 44

During neutralisation of the formic acid present in formaldehyde solution by shaking with the basic carbonate in a screw-capped bottle, the latter burst owing to pressure of liberated carbon dioxide. Periodical release of pressure should avoid this.

See other GAS EVOLUTION INCIDENTS, NEUTRALISATION INCIDENTS

Nitromethane

See Nitromethane: Formaldehyde

Other reactants

Yoshida, 1980, 346

MRH values for 14 combinations with oxidants are given, and are all high.

Peroxyformic acid MRH 5.69/100

See Peroxyformic acid: Organic materials

Phenol

1. Taylor, H. D. *et al., Major Loss Prevention in Process Industries*, (Symp. Ser. No. 34), 46, London, IChE, 1971
2. Anon., *Chem. Eng. News*, 1992, **70**(10), 7
3. Anon. *Chem. Eng. News*, 1997, **75**(38), 11
4. Starkie, A. *et al., Chem. in Brit.*, 1996, **32**(2), 35
5. Gustin, J.-L. *et al., J. Loss Prev.*, 1993, **6**(2), 103
6. Luo, K-M. *et al., J. Loss Prev. Process Ind.*, 2000, **13**, 91
7. U.S. Environmental Protection Agency, *Case Study EPA 550-F99-004*, 1999
8. Kumpisky, E., *Ind. Eng. Chem. Res.*, 1995, **34**(9), 3096
9. Kletz, T.A., *J. Haz. Mat.*, 2004, **115**(1-3), 1

At least 9 cases of catalysed plant-scale preparations of phenol—formaldehyde resin which ran away with sudden pressure development and failure of bursting disks or reactors are briefly mentioned. No details of process conditions are given [1]. Three loss of containment incidents, acid catalysed, are mentioned in [9]. A destructive incident, which must have developed the force of some kg of TNT, is reported without real detail [2]. Another fatal and destructive explosion when preparing phenol formaldehyde resins is reported [3]. The cause of this was apparently charging all reagents at once, contrary to procedure, then heating [7]. A photograph of the aftermath of a runaway polymerisation is reproduced [4]. A very thorough study of hazards of the phenol/formaldehyde polymerisation reaction, leading to calculations of emergency vent size, is given [5]. Another detailed study starts with DSC and reaction calorimetry, showing a heat of reaction up to 0.7 kJ/g (3 equivalents of 37% aqueous formaldehyde input) in a triple peaked thermogram, first order kinetics and some rate data. It then dives into several pages of mathematics, based on the assumption of thermal homogeneity within a reactor [extremely improbable with a runaway thermoset reaction increasing viscosity and coating cooled walls], to reach the conclusions that the cause of runaway is insufficient cooling and that the cure is more cooling capacity [6]. A more empirical study shows that the reaction goes at all pHs, but is slow between 2 & 7. In the operating region small changes in pH can give large changes in self-heating. It is suggested that neutralisation could form part of a quench procedure for incipient runaways [8].

See other POLYMERISATION INCIDENTS, RUNAWAY REACTIONS

Potassium permanganate

See Potassium permanganate: Formaldehyde

Sodium hydroxide

1. Ashby, E. C. *et al., J. Amer. Chem. Soc.*, 1993, **115**, 1171
2. Chrisope, D. R. *et. al., Chem. Eng. News.*, 1995, **73**(2), 2
3. Kapoor, S. *et al., J. Phys. Chem.*, 1995, **99**(18), 6857

In place of the well known Cannizzaro reaction (which is significantly exothermic) formaldehyde, at lower concentrations, produces hydrogen with alkalis, leading to possible pressurisation and ignition [1]. It has been demonstrated that this modified Cannizzaro reaction giving hydrogen can operate in real commercial situations (500 ppm formaldehyde, 1.5% sodium hydroxide). Caution and ventilated or inerted headspaces when storing alkaline formaldehyde containing products are advisable [2]. A detailed study of the kinetics and mechanism of hydrogen evolution has been published [3].

Water, Methanol, Air

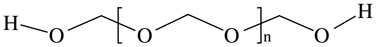
Anon., *Jahresbericht*, 1994, 73

An explosion is recorded, consequent upon welding a ladder to the wall of a half-full tank, which had not been inerted with nitrogen and was vented to atmosphere, containing a 37% formaldehyde solution stabilised with 5.6% methanol at 72°C. The flash point of this mixture in air is about 71°C, autoignition temperature 420°C: the head space ignited, killing two workers, injuring nine and blowing off the top of the tank.

See other ALDEHYDES, REDUCANTS

0416. Paraformaldehyde

[9002-81-7] **$(CH_2O)_n$**



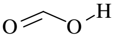
The dry finely powdered linear polymer is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

See other ALDEHYDES, REDUCANTS

0417. Formic acid (Methanoic acid)

[64-18-6] **CH_2O_2**



FPA H86, 1979; *HCS 1980*, 508

1. *BCISC Quart. Safety Summ.*, 1973, **44**, 18
2. Falconer, J. *et al., Proc. 2nd Int. Conf. Solid. Surf.*, 1974, 525
3. Anon., *Jahresber.*, 1981, 74
4. Reynolds, R. J., *DNA Repair*, 1981, **1(A)**, 11—21, NY, Dekker
5. Robertson, A. V., *Chem. Eng. News*, 1989, **67**(46), 2
6. Bond, J., *Loss Prev. Bull.*, 1983, **56**, 24

The slow decomposition in storage of 98—100% formic acid with liberation of carbon monoxide led to rupture of the sealed glass containers. In absence of gas leakage, a full 2.5 l bottle would develop a pressure of over 7 bar during 1 year at 25°C [1]. This has caused injury in laboratories. Formic acid is now often supplied in vented bottles, but unvented ones may still be met and should be vented by loosening the caps from time to time [5]. Explosive decomposition of formic acid on a clean nickel (1.1.0) surface was studied, using deuteroformic acid [2]. A full 1 l bottle of 96%

formic acid burst when the ambient temperature fell to —6°C overnight and the contents froze and expanded. Gas pressure from previous partial decomposition may also have contributed [3]. Hydrolysis of precipitated DNA with 97% acid at 180°C in sealed glass tubes is potentially hazardous because of rapid gas formation [4]. After tank storage, the decomposition has caused fatalities from carbon monoxide poisoning when tanks are entered for cleaning purposes without thorough prior ventilation, even with (ill fitting) breathing sets [6].
See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS

Aluminium
See Aluminium: Formic acid

Hydrogen peroxide
See Hydrogen peroxide: Oxygenated compounds

Hydrogen peroxide MRH 3.30/42
See Peroxyformic acid (references 5,6)

4-Hydroxy-3-methoxybenzaldehyde, Thallium(III) nitrate
See Thallium(III) nitrate: Formic acid, etc.

Nitric acid MRH 2.64/36
See Nitric acid: Formic acid

Nitric acid, Urea
See Nitric acid: Formic acid, Urea

Nitromethane MRH 5.69/100
See Nitromethane: Acids

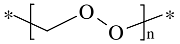
Other reactants
Yoshida, 1980, 100
MRH values calculated for 16 combinations, largely with oxidants, are given.

Palladium—carbon catalyst
Freifelder, 1971, 188
Addition of dry catalyst to 98% formic acid used as a hydrogenation solvent can be extremely hazardous, because hydrogen is released by decomposition of the acid. Addition of acid to the water-wetted catalyst is safer.
See other GAS EVOLUTION INCIDENTS, HYDROGENATION INCIDENTS

Phosphorus pentaoxide
Muir, G. D., private comm., 1968
Attempted dehydration of 95% acid to anhydrous formic acid caused rapid evolution of carbon monoxide.
See other GAS EVOLUTION INCIDENTS

Sodium hypochlorite
See Sodium hypochlorite: Formic acid
See other ORGANIC ACIDS, REDUCANTS

0418. Formaldehyde oxide polymer (Poly(dioxymethylene))
[107981-97-5] **$(CH_2O_2)_n$**

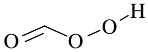


Lapalme, R. *et al., Can. J. Chem.*, 1979, **57**, 3272

The dry peroxide polymer (formed in ozonisation of vinyl acetate, and possibly a dioxirane polymer) is a shock-sensitive explosive, which needs care in handling.

See other POLYPEROXIDES

0419. Peroxyformic acid (Methaneperoxoic acid)
[107-32-4] **CH_2O_3**



1. Greenspan, F. P., *J. Amer. Chem. Soc.*, 1946, **68**, 907
2. D'Ans, J. *et al., Ber.*, 1915, **48**, 1136
3. Weingartshofer, A. *et al., Chem. Eng. News*, 1952, **30**, 3041
4. Swern, 1970, Vol. 1, 337
5. Isard, A. *et al., Chemical Tech.*, 1974, **4**, 380
6. Anon., *Chem. Eng. News*, 1950, **28**, 418
7. Stull, 1977, 19

Peroxyformic acid solutions are unstable and undergo a self-accelerating exothermic decomposition at ambient temperature [1]. An 80% solution exploded at 80—85°C [2]. A small sample of the pure vacuum-distilled material cooled to below —10°C exploded when the flask was moved [3]. Though the acid has occasionally been distilled, this is an extremely dangerous operation (it is formally the redox compound formyl hydroperoxide) [4]. During preparation of the acid by a patented procedure involving interaction of formic acid with hydrogen peroxide in the presence of metaboric acid, an explosion occurred which was attributed to spontaneous separation of virtually pure peroxyformic acid [5]. Following an incident in which a 1:1 mixture of formic acid and 90% hydrogen peroxide had exploded violently when handled after use as an oxidant [6], it was calculated that the (redox) decomposition exotherm (1.83 kJ/g of acid) would attain an adiabatic reaction temperature of 1800°C with a 22-fold increase in pressure in a closed container [7].

Chlorine

See Chlorine: Chloromethane

Metals, or Metal oxides

D'Ans, J. *et al., Ber.*, 1915, **48**, 1136

Violence of reaction depends on concentration of acid and scale and proportion of reactants. The following observations were made with additions to 2—3 drops of ca. 90% acid. Nickel powder, becomes violent; mercury, colloidal silver and thallium powder readily cause explosions; zinc powder causes a violent explosion immediately. Iron powder is ineffective alone, but a trace of manganese dioxide promotes deflagration. Barium peroxide, copper(I) oxide, impure chromium trioxide, iridium dioxide, lead dioxide, manganese dioxide and vanadium pentoxide all cause violent decomposition, sometimes accelerating to explosion. Lead(II) oxide, lead(II),(IV) oxide and sodium peroxide all cause an immediate violent explosion.

Non-metals

D'Ans, J. *et al., Ber.*, 1915, **48**, 1136

Impure carbon and red phosphorus are oxidised violently, and silicon, promoted by traces of manganese dioxide, is oxidised with ignition.

Organic materials

1. D'Ans, J. *et al., Ber.*, 1915, **48**, 1136
2. Anon., *Chem. Eng. News*, 1950, **28**, 418
3. Shanley, E. S., *Chem. Eng. News*, 1950, **28**, 3067
4. Öhlenschlager, A. *et al., Chem. Eng. News*, 1987, **65**(15), 2

Formaldehyde, benzaldehyde and aniline react violently with 90% performic acid [1]. An unspecified organic compound was added to the acid (preformed from formic acid and 90% hydrogen peroxide), and soon after the original vigorous reaction had subsided, the mixture exploded violently [2]: (see references 6,7 above). Reaction with alkenes is vigorously exothermic, and adequate cooling is necessary [3]. Reactions with performic acid can be more safely accomplished by slow addition of hydrogen peroxide to a solution of the compound in formic acid, so that the peroxyacid is used as it is formed. Adequate safety screens should be used with all peracid preparations [3]. After the hydroxylation of *trans*-2-pentanoic acid with performic acid according to a published general procedure, while formic acid and water were being distilled off under vacuum at 45°C, a violent explosion occurred. This was attributed to decomposition of unreacted performic acid [4].

Sodium nitrate

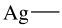
D'Ans, J. *et al., Ber.*, 1915, **48**, 1139

The salt may lead to explosive decomposition of the peroxy acid.

See other PEROXYACIDS, REDOX COMPOUNDS

0420. Methylsilver

[75993-65-6] **CH_3Ag**



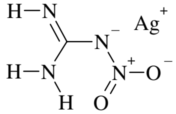
Thiele, H., *Z. Elektrochem.*, 1943, **49**, 426

Prepared at —80°C, the addition compound with silver nitrate decomposes explosively on warming to —20°5C.

See other ALKYLMETALS

0421. Silver nitroguanidide

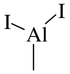
[ ] **$CH_3AgN_4O_2$**



See Nitroguanidine
See other SILVER COMPOUNDS

0422. Methylaluminium diiodide

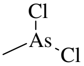
[2938-46-7] **CH_3AlI_2**



Nitromethane
See Nitromethane: Alkylmetal halides
See other ALKYLALUMINIUM HALIDES

0423. Dichloromethylarsine

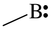
[593-89-5] **CH_3AsCl_2**



Chlorine
See Chlorine: Dichloro(methyl)arsine
See other ALKYLNON-METAL HALIDES

0424. Methylborylene

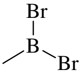
[62785-41-5] **CH_3B**



Preparative hazard
See Dibromomethylborane: Sodium—potassium alloy (next below)
See related ALKYLBORANES

0425a. Dibromomethylborane

[17933-16-3] **CH_3BBr_2**



Nöth, H. *et al., Inorg. Synth.*, 1983, **22**, 223
It may ignite in air if warm, or if the heat of oxidation or hydrolysis cannot be dissipated.
See other SELF-HEATING AND IGNITION INCIDENTS

Sodium—potassium alloy

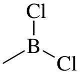
Van der Kerk, S. M. *et al., Polyhedron*, 1983, **2**, 1337

Use of potassium graphite or caesium graphite to generate methylborylene is uneventful, while use of sodium—potassium alloy (1:5 mol) caused an explosion in 2 out of 5 attempts.

See other ALKYLHALOBORANES

0425b. Dichloro(methyl)borane (Methylborondichloride)

[7318-78-7] **CH_3BCl_2**



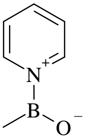
Rossiter, A., www.dukenews.duke.edu 1998

An explosion in a beaker when distilling this compound is reported. The circumstances are unclear – beakers are not normal distillation apparatus but a very probable vessel for reaction with water, by accident or intent.

See also Dibromomethylborane

0426. Methaneboronic anhydride—pyridine complex

[79723-21-0] **$CH_3BO.C_5H_5N$**



1. Mattesson, D. S. *et al., J. Org. Chem.*, 1964, **29**, 3399
2. Mattesson, D. S. *et al., Organometallics*, 1982, **1**, 27

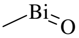
The published procedure [1] for preparing the complex failed to note that the organic extracts will ignite spontaneously if exposed to air for a few seconds during workup. Inert blanketing with argon is essential throughout, and the preparation is hazardous on the scale described. Ignition probably arises from by-product trimethylborane [2].

See other AUTOIGNITION INCIDENTS

See related ACID ANHYDRIDES

0427. Methylbismuth oxide (Methyloxobismuthine)

[ ] **CH_3BiO**



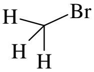
Marquardt, A., *Ber.*, 1887, **20**, 1522

It ignites on warming in air.

See related ALKYLMETALS

†0428. Bromomethane (Methyl bromide)

[74-83-9] **CH_3Br**



(*MCA SD-35*, 1968); *HCS 1980*, 641

1. *MCA SD-35*, 1968
2. *MCA Case History No. 746*

Though bromomethane is used as a fire extinguishant, it does in fact form difficultly flammable mixtures between 10 and 15% (13.5—14.5% but also 8.6—20% have been noted), the limits in oxygen, or under pressure, being wider [1][2].

See entry FLASH POINTS (reference 19)

Aluminium

Lambert, P. G., *Chem. and Ind.*, 1990, (18), 562

Specially bottled methyl bromide, in an aluminium cylinder under nitrogen pressure, disgorged a black sludge when liquid was discharged. Inversion and venting, to blow free the line, gave a burst of flame from the vent. It is presumed that corrosion of the cylinder produced pyrophoric aluminium alkyls.

See Trimethylaluminium; Aluminium: halocarbons

See other CORROSION INCIDENTS, METAL—HALOCARBON INCIDENTS

Dimethyl sulfoxide

See Trimethylsulfoxonium bromide

Ethylene oxide

See Ethylene oxide: Air, Bromomethane

Metals

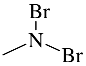
MCA Case History No. 746 and addendum

Metallic components of zinc, aluminium and magnesium (or their alloys) are unsuitable for service with bromomethane because of the formation of pyrophoric Grignard-type compounds. The Case History attributes a severe explosion to ignition of a bromomethane—air mixture by pyrophoric methylaluminium bromides produced by corrosion of an aluminium component.

See other CORROSION INCIDENTS, HALOALKANES, METAL—HALOCARBON INCIDENTS

0429. *N,N*-Dibromomethylamine

[10218-83-4] **CH_3Br_2N**



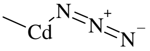
Cooper, J. C. *et al., Explosivstoffe*, 1969, **17**(6), 129—130

Like the dichloro analogue, it appears to be more sensitive to impact or shock than *N*-chloromethylamine.

See other N-HALOGEN COMPOUNDS

0430. Methylcadmium azide

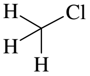
[7568-37-8] **CH_3CdN_3**



Dehnicke, K. *et al., J. Organomet. Chem.*, 1966, **6**, 298
Surprisingly it is thermally stable to 300°C, (cadmium azide is very heat sensitive) but is hygroscopic and very readily hydrolysed to explosive hydrogen azide.
See related METAL AZIDES

†0431. Chloromethane (Methyl chloride)

[74-87-3] **CH_3Cl**



(*MCA SD-40*, 1970); *FPA H68*, 1979; *HCS 1980*, 644

Aluminium
See Aluminium: Halocarbons

Aluminium chloride, Ethylene
See Ethylene: Aluminium chloride

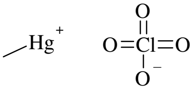
Interhalogens
See Bromine trifluoride: Halogens, etc.
Bromine pentafluoride: Hydrogen-containing materials

Metals
MCA SD-40, 1970
In presence of catalytic amounts of aluminium chloride, powdered aluminium and chloromethane interact to form pyrophoric trimethylaluminium. Chloromethane may react explosively with magnesium, or potassium, sodium or their alloys. Zinc probably reacts similarly to magnesium.
See Aluminium: Halocarbons
METAL—HALOCARBON INCIDENTS
Sodium: Halocarbons
See other CATALYTIC IMPURITY INCIDENTS

Other reactants
Yoshida, 1980, 366
MRH values calculated for 13 combinations with oxidants are given.
See other HALOALKANES

0432. Methylmercury perchlorate

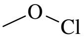
[40661-97-0] **CH_3ClHgO_4**



Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 214
On rubbing with a glass rod, a sample exploded violently. As the explosion could not be reproduced with a metal rod, initiation by static electricity was suspected.
See other STATIC INITIATION INCIDENTS
See related METAL PERCHLORATES

0433. Methyl hypochlorite

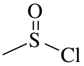
[593-78-2] **CH_3ClO**



Sandmeyer, T., *Ber.*, 1886, **19**, 859
The liquid could be gently distilled (12°C) but the superheated vapour readily and violently explodes, as does the liquid on ignition.
See other HYPOHALITES

0434. Methanesulfinyl chloride

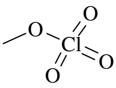
[676-85-7] **CH_3ClOS**



Douglass, I. B. *et al., J. Org. Chem.*, 1964, **29**, 951
A sealed ampoule burst after shelf storage for several months. Store only under refrigeration.
See other ACYL HALIDES

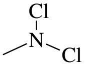
0435. Methyl perchlorate

[17043-56-0] **CH_3ClO_4**



Sidgwick, 1950, 1236
The high explosive instability is due in part to the covalent character of the alkyl perchlorates, and also to the excess of oxygen in the molecule over that required to combust completely the other elements present (i.e. a positive oxygen balance).
See other ALKYL PERCHLORATES

0436. *N,N*-Dichloromethylamine
[7651-91-4] **CH_3Cl_2N**



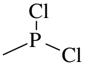
Calcium hypochlorite, or Sodium sulfide, or Water

1. Bamberger, E. *et al., Ber.*, 1895, **28**, 1683
2. Okon, K. *et al., Chem. Abs.*, 1960, **54**, 17887

A mixture with water exploded violently on warming [1]. Contact with solid sodium sulfide or distillation over calcium hypochlorite also caused explosions [2].

See other N-HALOGEN COMPOUNDS

0437. Dichloromethylphosphine
[676-83-5] **CH_3Cl_2P**



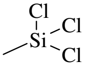
Bis(2-hydroxyethyl)methylphosphine

Piccinni-Leopardi, C. *et al., J. Chem. Soc., Perkin Trans. 2*, 1986, 91

Cyclo-condensation of the 2 components gives 2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclooctane, and its subsequent distillation (65—68°C/0.07 mbar) must be effected with bath temperatures below 120°C to avoid explosion.

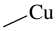
See other ALKYLHALOPHOSPHINES

†0438. Methyltrichlorosilane
[75-79-6] **CH_3Cl_3Si**



See other ALKYLHALOSILANES

0439. Methylcopper
[1184-53-8] **CH_3Cu**



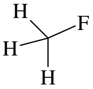
1. Coates, 1960, 348
2. Ikariya, T. *et al., J. Organomet. Chem.*, 1974, **72**, 146

The dry solid is very impact-sensitive and may explode spontaneously on being allowed to dry out at room temperature [1]. Methylcopper decomposes explosively at ambient temperature, and violently in presence of a little air [2].

See other ALKYLMETALS

†0440. Fluoromethane (Methyl fluoride)

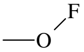
[593-53-3] **CH_3F**



See other HALOALKANES

0441. Methyl hypofluorite (Fluoroxymethane)

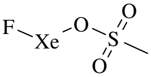
[36336-08-0] **CH_3FO**



Appelman, E. *et al., J. Amer. Chem. Soc.*, 1991, **113**(7), 2648
This compound, the first known alkyl hypofluorite, was found to be stable but reactive at —120°C, but samples sometimes exploded on warming to cardice temperatures (—80°C?).

0442. Xenon(II) fluoride methanesulfonate

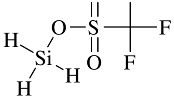
[ ] **CH_3FO_3SXe**



Wechsberg, M. *et al., Inorg. Chem.*, 1972, **11**, 3066
The solid explodes on warming from 0°C to ambient temperature.
See other XENON COMPOUNDS

0443. Silyl trifluoromethanesulfonate

[2923-28-6] **$CH_3F_3O_3SSi$**



Bassindale, A. R. *et al., J. Organomet. Chem.*, 1984, **271**, C2
It cannot be isolated pure by distillation at ambient pressure as it disproportionates to spontaneously flammable silane.
See related SULFUR ESTERS

0444. Iodomethane (Methyl iodide)

[74-88-4] **CH_3I**

HCS 1980, 562

Oxygen

Antonik, S., *Bull. Soc. Chim. Fr.*, 1982, **3—4**, 128—133

Second stage ignition during oxidation/combustion of iodomethane in oxygen at 300—500°C was particularly violent, occasionally causing fracture of the apparatus, and was attributed to formation and decomposition of a periodic species.

Silver chlorite

See Silver chlorite: Iodoalkanes

Sodium

1. Anon., *J. Chem. Educ.*, 1966, **43**, A236
2. Braidech, M. M., *J. Chem. Educ.*, 1967, **44**, A324

The first stage of a reaction involved the addition of sodium dispersed in toluene to a solution of adipic ester in toluene. The subsequent addition of iodomethane (b.p. 42°C) was too fast and vigorous boiling ejected some of the flask contents. Exposure of sodium particles to air caused ignition, and a violent toluene—air explosion followed [1]. When a reagent as volatile and reactive as iodomethane is added to a hot reaction mixture, controlled addition, and one or more wide-bore reflux condensers are essential. A similar incident involving benzene was also reported [2].

See Sodium: Halocarbons

Trialkylphosphines

Houben-Weyl, 1963, Vol. 12.1, 79

In the absence of a solvent, quaternation of trialkylphosphines with methyl iodide may proceed explosively.

See other HALOALKANES

0445. Methylmagnesium iodide (Iodomethylmagnesium)

[917-64-6] **CH_3IMg**

Thiophosphoryl chloride

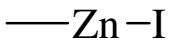
See Tetramethyldiphosphane disulfide

Vanadium trichloride

See Vanadium trichloride: Methylmagnesium iodide

See other ALKYLMETAL HALIDES, GRIGNARD REAGENTS

0446. Methylzinc iodide (Iodomethylzinc)
[18815-73-1] **CH_3IZn**



Nitromethane

See Nitromethane: Alkylmetal halides

See other ALKYLMETAL HALIDES

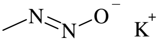
0447. Methylpotassium
[17814-73-2] **CH_3K**

Weiss, E. *et al., Angew. Chem. (Intern. Ed.)*, 1968, **7**, 133

The dry material is highly pyrophoric.

See other ALKYLMETALS

0448. Potassium methanediazoate (Potassium methyldiazeneoxide)
[19416-93-4] **CH_3KN_2O**



Water

Hantzsch, A. *et al., Ber.*, 1902, **35**, 901

Interaction with water is explosively violent.

See other N—O COMPOUNDS

See related ARENEDIAZOATES

0449. Potassium methoxide
[865-33-8] **CH_3KO**

It may ignite in moist air.

See entry METAL ALKOXIDES

Arsenic pentafluoride, Benzene

See Arsenic pentafluoride: Benzene, etc.

0450. Potassium methylselenide
[54196-34-8] **CH_3KSe**

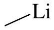
2-Nitroacetophenone

See 2-Nitroacetophenone: Potassium methylselenide

See related METAL ALKOXIDES

0451. Methyllithium

[917-54-4] **CH_3Li**



Sidgwick, 1950, 71

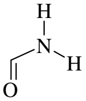
Ignites and burns brilliantly in air. The commercial solution in diethyl ether is also pyrophoric.

See ALKALI-METAL DERIVATIVES OF HYDROCARBONS

See other ALKYLMETALS

0452. Formamide

[75-12-7] **CH_3NO**



HCS 1980, 507; *RSC Lab. Hazards Data Sheet No. 58*, 1987

Aluminium, Ammonium nitrate, Calcium nitrate

See Calcium nitrate: Aluminium, etc.

Di-*tert*-butyl hyponitrite

See Di-*tert*-butyl hyponitrite: Formamides

Iodine, Pyridine, Sulfur trioxide

Anon., *J. Chem. Educ.*, 1973, **50**, A293

Bottles containing a modified Karl Fischer reagent with formamide replacing methanol developed gas pressure during several months and burst. No reason was apparent, but slow formation of sulfuric acid, either by absorption of external water or by dehydration of some of the formamide to hydrogen cyanide, and liberation of carbon monoxide from the formamide seems a likely sequence.

See other GAS EVOLUTION INCIDENTS

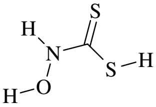
Organozinc compounds

Mistryukov, E. A. *et al., Mendeleev Comm.*, 1993, (6) 242

Adding formamide to a reaction mixture of allylzinc bromide and a ketone as a proton source for a Barbier reaction in ether or tetrahydrofuran gave uncontrollable explosion-like reaction. The reaction proceeded smoothly when starting from zinc dust and allyl bromide, with both formamide and the ketone in situ.

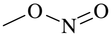
0453. *N*-Hydroxydithiocarbamic acid

[66427-01-8] **CH_3NOS_2**



Voigt, C. W. *et al., Z. Anorg. Chem.*, 1977, **437**, 233—236
The free acid is unstable and may decompose explosively at sub-zero temperatures.
See other N—O COMPOUNDS, ORGANIC ACIDS

†0454. Methyl nitrite
[624-91-9] **CH_3NO_2**

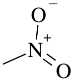


NSC 693, 1982; *HCS 1980*, 687

Rüst, 1948, 285
Explodes on heating, more powerfully than the ethyl homologue.

Other reactants
Yoshida, 1980, 14
MRH values calculated for 16 combinations, largely with oxidants, are given.
See other ALKYL NITRITES, N—O COMPOUNDS

0455. Nitromethane
[75-52-5] **CH_3NO_2**



1. *HCS 1980*, 687
2. McKitterick, D. S. *et al., Ind. Eng. Chem. (Anal. Ed.)*, 1938, **10**, 630
3. Makovky, A. *et al., Chem. Rev.*, 1958, **58**, 627
4. Travis, J. R., *Los Alamos Rept. DC 6994*, Washington, USAEC, 1965
5. Sorbe, 1968, 148
6. Lieber, C. O., *Chem. Ing. Tech.*, 1978, **50**, 695—697
7. Perche, A. *et al., J. Chem. Res.*, 1979, (S) 116; (M) 1555—1578
8. Lewis, D. J., *Haz. Cargo Bull.*, 1983, **4**(9), 36—38
9. Stull, 1977, 20
10. Anon., *Jahresber.*, 1984, 66—67
11. Coetzee, J. F. *et al., Pure Appl. Chem.*, 1986, **58**, 1541—1545
12. Brewer, K. R., *J. Org. Chem.*, 1988, **53**, 3776—3779
13. Piermanini, G. J. *et al., J. Phys. Chem.*, 1989, **93**(1), 457—462
14. Dick, J. J., *J. Phys. Chem.*, 1993, **97**(23), 6193
15. Ullmann, 1991, A 17, 405/6

Hazardous properties and handling procedures are summarised [1]. Conditions under which it may explode by detonation, heat or shock were determined. It was concluded that it is potentially very explosive and precautions are necessary to prevent its exposure to severe shock or high temperatures in use [2]. Later work, following two rail tank explosions, showed that shock caused by sudden application of gas pressure, or sudden forced flow through restrictions, could detonate the liquid. The stability and decomposition of nitromethane relevant to use as a rocket fuel are also reviewed [3]. The role of discontinuities in the initiation of shock-compressed nitromethane has been evaluated experimentally [4]. It explodes at about 230°C [5]. The role of pressure waves producing local resonance heating in bubbles and leading to detonation has been studied [6], as have the effects of nitrogen oxide, nitrogen dioxide and formaldehyde upon pyrolytic decomposition of nitromethane [7]. Bulk shipment in rail tanks is now permitted for solutions in appropriate diluents [8].

The heat of decomposition (238.4 kJ/mol, 3.92 kJ/g) has been calculated to give an adiabatic product temperature of 2150°C accompanied by a 24-fold pressure increase in a closed vessel [9]. During research into the Friedel-Crafts acylation reaction of aromatic compounds (components unspecified) in nitrobenzene as solvent, it was decided to use nitromethane in place of nitrobenzene because of the lower toxicity of the former. However, because of the lower boiling point of nitromethane (101°C, against 210°C for nitrobenzene), the reactions were run in an autoclave so that the same maximum reaction temperature of 155°C could be used, but at a maximum pressure of 10 bar. The reaction mixture was heated to 150°C and maintained there for 10 minutes, when a rapidly accelerating increase in temperature was noticed, and at 160°C the lid of the autoclave was blown off as decomposition accelerated to explosion [10]. Impurities present in the commercial solvent are listed, and a recommended purification procedure is described [11]. The thermal decomposition of nitromethane under supercritical conditions has been studied [12]. The effects of very high pressure and of temperature on the physical properties, chemical reactivity and thermal decomposition of nitromethane have been studied, and a mechanism for the bimolecular decomposition (to ammonium formate and water) identified [13]. Solid nitromethane apparently has different susceptibility to detonation according to the orientation of the crystal, a theoretical model is advanced [14]. Nitromethane actually finds employment as an explosive [15].

See Acetone below, or Haloforms below

Acetone

Varob'ev, A. A., *Chem. Abs.*, 1981, **94**, 49735

Mixtures can be detonated (title only translated).

Acids, or Bases

Makovky, A. *et al., Chem. Rev.*, 1958, **58**, 631

Addition of bases or acids to nitromethane renders it susceptible to initiation by a detonator. These include aniline, diaminoethane, iminobispropylamine, morpholine, methylamine, ammonium hydroxide, potassium hydroxide, sodium carbonate, and formic, nitric, sulfuric or phosphoric acids.

See 1,2-Diaminoethane, *N*,2,4,6-Tetranitro-*N*-methylamine, below

Alkalis

Ullmann, 1991, A 17, 405/6

It will form *aci*-nitromethanoate salts, which are sensitive explosives when dry, and may form methazonates (salts of nitroacetaldehyde oxime) which are still more explosive.

See Sodium *aci*-nitromethanide, 2-Nitroacetaldehyde oxime

Alkylmetal halides

Traverse, G., US Pat. 2 775 863, 1957

Contact with R_mMX_n (R is methyl, ethyl; M is aluminium, zinc; X is bromide, iodide) causes ignition. Diethylaluminium bromide, dimethylaluminium bromide, ethylaluminium bromide iodide, methylzinc iodide and methylaluminium diiodide are claimed as specially effective.

Aluminium chloride

See Aluminium chloride—nitromethane

Aluminium chloride, Ethylene

See Ethylene: Aluminium chloride

Aluminium powder MRH 9.33/23

Kato, Y. *et al., Chem. Abs.*, 1979, **91**, 159867

Increase in concentration of aluminium powder in a mixture with poly(methyl methacrylate) increases the sensitivity to detonation.

Ammonium salts, Organic solvents

Runge, W. F. *et al.*, US Pat. 3 915 768, 1975

Presence of, for example, 5% of methylammonium acetate and 5% of methanol sensitises nitromethane to shock-initiation.

Bis(2-aminoethyl)amine

1. Runge, W. F. *et al.*, US Pat. 3 798 902, 1974
2. Walker, F. E., *Acta Astronaut.*, 1979, **6**, 807—813

Explosive solutions of nitromethane in dichloromethane, sensitised by addition of 10—12% of the amine, retained their sensitivity at —50°C [1]. Presence of 0—5% of the triamine considerably increases detonation sensitivity of nitromethane [2].

Boron trifluoride etherate, Silver oxide

See Silver tetrafluoroborate

Bromine

See Bromine: Nitromethane

Calcium hypochlorite

See Calcium hypochlorite: Nitromethane

Carbon Disulphide

Editor's comments

Salts of the reaction product, nitroethanedithioic acid, are intermediates in manufacture of pharmaceuticals. They are explosive and isolation is to be avoided. The free acid will surely be unstable, but not necessarily explosive.

1,2-Diaminoethane, *N*,2,4,6-Tetranitro-*N*-methylaniline

MCA Case History No. 1564

During preparations to initiate the explosion of nitromethane sensitised by addition of 20% of the diamine, accidental contact of the liquid mixture with the solid 'tetryl' detonator caused ignition of the latter.

See Acids, or Bases, above

Formaldehyde

Noland, W. E., *Org. Synth.*, 1961, **41**, 69

Interaction of nitromethane and formaldehyde in presence of alkali gives not only 2-nitroethanol, but also di- and tri-condensation products. After removal of the 2-nitroethanol by vacuum distillation, the residue must be cooled before admitting air into the system to prevent a flash explosion or violent fume-off.

Haloforms

Presles, H. N. *et al., Acta Astronaut.*, 1976, **3**, 531—540

Mixtures with chloroform or bromoform are detonable.

Hydrazine, Methanol

Forshey, D. R. *et al., Explosivstoffe*, 1969, **17**(6), 125—129

Addition of hydrazine strongly sensitises nitromethane and its mixtures with methanol to detonation.

Hydrocarbons

1. Watts, C. E., *Chem. Eng. News*, 1952, **30**, 2344
2. Makovky, A. *et al., Chem. Rev.*, 1958, **58**, 631

Nitromethane may act as a mild oxidant, and should not be heated with hydrocarbons or readily oxidisable materials under confinement [1]. Explosions may occur during cooling of such materials heated to high temperatures and pressures [2]. Mixtures of nitromethane and solvents which are to be heated above the b.p. of nitromethane should first be subjected to small-scale explosive tests [2].

Hydrocarbons, Oxygen

See Oxygen: Hydrocarbons, Promoters

Lithium perchlorate MRH 5.69/43

1. Titus, J. A., *Chem. Eng. News*, 1971, **49**(23), 6
2. 'Nitroparaffin Data Sheet TDS 1' New York, Comm. Solvents Corp., 1965
3. Egly, R. S., *Chem. Eng. News*, 1973, **51**(6), 30

Explosions which occurred at the auxiliary electrode during electro-oxidation reactions in nitromethane—lithium perchlorate electrolytes, may have been caused by lithium fulminate. This could have been produced by formation of the lithium salt of nitromethane and subsequent dehydration to the fulminate [1], analogous to the known formation of mercury(II) fulminate [2]. This explanation is not considered tenable, however [3].

Lithium tetrahydroaluminate

1. Nystrom, R. F. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 3739
2. Wollweber, H. *et al.*, private comm., 1988

Addition of nitromethane to ethereal lithium tetrahydroaluminate solution at ambient temperature gave an explosively violent rection [1], and this was confirmed when addition of 0.5 ml of dry nitromethane to 10 ml of reducant solution led, after 30 s, to a violent explosion which pulverised the flask [2]. The violence of the explosion suggests that lithium *aci*-nitromethanide (or possibly lithium fulminate) may have been involved.

See Sodium hydride, below

See other aci-NITRO SALTS

Metal oxides

See other NITROALKANES: Metal oxides

Molecular sieve

1. Wollweber, H., private comm., 1979
2. Bretherick, L., *Chem. & Ind.*, 1979, 532

Nitromethane was dried and stored in a flask over 13X (large-pore) molecular sieve, and when a further portion of freshly activated sieve was added after several weeks, the contents erupted and ignited, breaking the flask [1]. This was attributed to slow formation of sodium *aci*-nitromethanide from the zeolitic sodium ions, which then decomposed in the exotherm arising from adsorption of nitromethane on the freshly activated sieve. Use of a small-pore (3A or 4A) sieve which would exclude nitromethane from the internal channels and greatly reduce the contact with sodium ions should avoid this problem. The possibility of other problems arising from slow release or exchange of ionic species under virtually anhydrous conditions during long term use of molecular sieves was noted [2].

See other MOLECULAR SIEVE INCIDENTS

Nickel

Benziger, J. B., *Appl. Surface Sci.*, 1984, **17**, 309—323

Decomposition of nitromethane on the (111) face of nickel has been studied.

Nitric acid MRH 6.19/38

See Nitric acid: Nitromethane

Other reactants

Yoshida, 1980, 278

MRH values calculated for 17 combinations, largely with oxidants, are given.

Silver nitrate

Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 336

Aqueous silver nitrate may react to form silver fulminate.

Sodium hydride

1. Pearson, A. J. *et al., J. Organomet. Chem.*, 1980, **202**, 178
2. Johnson, B. F. G. *et al., J. Organomet Chem.*, 1981, **204**, 221—228

Generation of sodium *aci*-nitromethanide by adding de-oiled sodium hydride powder to nitromethane in THF becomes violent at 40°C [1], and if the solvent is omitted, too fast addition of the hydride leads to a series of small explosions [2].

See Sodium *aci*-nitromethanide

Trimethylsilyl iodide

Voronkov, M. G. *et al., Zh. Obshch. Khim.*, 1989, **59**(5), 1055. (*Chem. Abs.,* **112**, 77304)

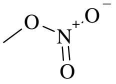
Reaction of the silane with nitromethane is explosive, probably by intermediacy of fulminic acid (a dehydration product of nitromethane).

Uronium perchlorate

See Uronium perchlorate: Organic materials

See other C—NITRO COMPOUNDS, NITROALKANES

0456. Methyl nitrate
[598-58-3] **CH_3NO_3**



1. Kit and Evered, 1960, 268
2. Black. A. P. *et al., Org. Synth.*, 1943, Coll. Vol. 2, 412
3. Goodman, H. *et al., Combust. Flame*, 1972, **19**, 157
4. Griffiths, J. F. *et al., Combust. Flame*, 1982, **45**, 54—66
5. Stull, 1977, 20

It has high shock- and thermal sensitivity, exploding at 65°C, and is too sensitive for use as a rocket mono-propellant [1]. Conditions during preparation of the ester from methanol and mixed nitric—sulfuric acids are fairly critical, and explosions may occur if it is suddenly heated or distilled in presence of acid [2]. Spontaneous ignition or explosion of the vapour at 250—316°C in presence of gaseous diluents [3], and the mechanism of exothermic decomposition and ignition [4] have been studied. The rather high decomposition exotherm (153.8 kJ/mol, 4.42 kJ/g) would raise the products to an adiabatic temperature approaching 2600°C, with a 31-fold pressure increase in a closed system [5].

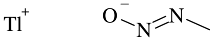
Other reactants

Yoshida, 1980, 207

Of the MRH values calculated for 11 combinations, that with magnesium was most energetic at 8.70/38.

See other ALKYL NITRATES

0457. Thallium(I) methanediazoate (Thallium *N*-nitrosomethylamide)
[113925-83-0] **CH_3N_2OTl**



1. Keefer, L. K. *et al., J. Amer. Chem. Soc.*, 1988, **110**, 2800—2806, and footnote 20
2. Burns, M. E., private comm., 1985

It appears to be a stable covalent highly crystalline compound (unlike other metal methanediazoates). Alkanediazoates are easily converted to diazoalkanes, so should be regarded as capable of detonation. (Though named by the author as a methanediazoate, it is indexed and registered in *CA* as a nitrosomethylamide salt) [1]. A sample of the freshly synthesised compound was dissolved in dichlorodideuteromethane and sealed into an NMR tube. Four days later, when the tube was being opened for recovery of the sample, the tube exploded. This was attributed to diazomethane formation, possibly from reaction with traces of moisture sealed into the tube [2].

See other HEAVY METAL DERIVATIVES, N—O COMPOUNDS

0458. Methyl azide

[624-90-8] **CH_3N_3**

$$—N=\overset{+}{N}=N^{-}$$

1. *MCA Case History No. 887*
2. Boyer, J. H. *et al., Chem. Rev.*, 1954, **54**, 323
3. Burns, M. E. *et al., Chem. Eng. News*, 1984, **62**(2), 2

The product, prepared by interaction of sodium azide with dimethyl sulfate and sodium hydroxide, exploded during concurrent vacuum distillation. The explosion was attributed to formation and co-distillation with the product of hydrogen azide, owing to excursion of the pH to below 5 during the preparation. Free hydrogen azide itself is explosive, and it may also have reacted with mercury in a manometer to form the detonator mercuric azide [1]. Methyl azide is stable at ambient temperature, but may detonate on rapid heating [2]. A further explosion during the preparation as above led to incorporation of bromothymol blue in the reaction system to give a visible indication of pH in the generation flask [3].

Mercury

Currie, C. L. *et al., Can. J. Chem.*, 1963, **41**, 1048

Presence of mercury in methyl azide markedly reduces the stability towards shock or electric discharge.

Methanol

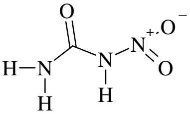
Grundman, C. *et al., Angew. Chem.*, 1950, **62**, 410

In spite of extensive cooling and precautions, a mixture of methyl azide, methanol and dimethyl malonate exploded violently while being sealed into a Carius tube. The vapour of the azide is very easily initiated by heat, even at low concentrations.

See other ORGANIC AZIDES

0459. Nitrourea

[556-89-8] **$CH_3N_3O_3$**

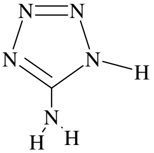


1. Urbanski, 1967, Vol. 3, 34
2. Medard, L., *Mem. Poudres*, 1951, **33**, 113—123; (English transl., HSE 11292, available from HSE/LIS, 1986)

A rather unstable explosive material, insensitive to heating or impact, which gives mercuric and silver salts which are rather sensitive to impact [1]; further detailed data are available [2].

See other N—NITRO COMPOUNDS

0460. 5-Aminotetrazole
[4418-61-5] **CH_3N_5**



Nitrous acid

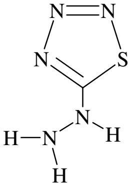
1. Elmore, D. T., *Chem. Brit.*, 1966, **2**, 414
2. Thiele, J., *Ann.*, 1892, **270**, 59
3. Gray, E. J. *et al., J. Chem. Soc., Perkin Trans. 1*, 1976, 1503
4. Cawkill, E. *et al., J. Chem. Soc., Perkin Trans. 1*, 1979, 727

Diazotised 5-aminotetrazole is unstable under the conditions recommended for its use as a biochemical reagent. While the pH of the diazotised material (the cation of which contains 87% nitrogen) at 0°C was being reduced to 5 by addition of potassium hydroxide, a violent explosion occurred [1]. This may have been caused by a local excess of alkali causing the formation of the internal salt, 5-diazoniotetrazolide, which will explode in concentrated solution at 0°C [2]. The diazonium chloride is also very unstable in concentrated solution at 0°C. Small-scale diazotisation (2g of amine) and susequent coupling at pH 3 with ethyl cyanoacetate to prepare ethyl 2-cyano-(1*H*-tetrazol-5-ylhydrazono)acetate proceeded uneventfully, but on double the scale a violent explosion occurred [3]. The importance of adequate dilution of the reaction media to prevent explosions during diazotisation is stressed [4].

See DIAZONIUM SALTS

See other HIGH-NITROGEN COMPOUNDS, TETRAZOLES

0461. 5-Hydrazino-1,2,3,4-thiatriazole
[99319-30-9] **CH_3N_5S**



Martin, D., *Z. Chem.*, 1985, **25**(4), 136—137

The explosive title compound was not isolated after preparation from thiocarbazide and nitrous acid, but was condensed with various ketones to give the hydrazones.

See other HIGH-NITROGEN COMPOUNDS, N—S COMPOUNDS

See related TRIAZOLES

0462. Methylsodium

[18356-02-0] **CH_3Na**

Schlenk, W. *et al., Ber.*, 1917, **50**, 262
Ignites immediately in air. The tendency to ignition decreases with ascent of the homologous series of alkylsodiums.
See other ALKYLMETALS

0463. Sodium methoxide

[124-41-4] **CH_3NaO**

1. *HCS 1980*, 850
2. *See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

It may ignite in moist air. Hazardous properties and handling procedures are summarised [1]. Energy of decomposition (in range 410—460°C) measured as 0.77 kJ/g [2].

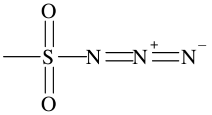
Chloroform
See Chloroform: Sodium methoxide

4-Chloronitrobenzene
See 4-Chloronitrobenzene: Sodium methoxide

Perfluorocyclopropene
See FLUORINATED CYCLOPROPENYL METHYL ETHERS
See other METAL ALKOXIDES

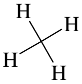
0464. Methanesulfonyl azide

[1516-70-7] **$CH_3N_3O_2S$**



Brown, R. *et al., Chem. Brit.*, 1994, **30**(6), 470
Gram quantities of the azide have twice detonated, once during distillation, the second time also possibly due to localised overheating. It is stated that there was hitherto only a general warning of possible explosivity.
See other ACYL AZIDES

†0465. Methane
[74-82-8] **CH_4**



FPA H59, 1977; *HCS 1980*, 627 (cylinder)

Halogens, or Interhalogens

See Bromine pentafluoride: Hydrogen-containing materials
Chlorine trifluoride: Methane
Chlorine: Hydrocarbons
Fluorine: Hydrocarbons
Iodine heptafluoride: Carbon, etc.

Other reactants

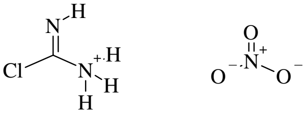
Yoshida, 1980, 361

MRH values calculated for 12 combinations with oxidants are given.

Oxidants

See Dioxygen difluoride: Various materials
Dioxygenyl tetrafluoroborate: Organic materials
Oxygen (Liquid): Hydrocarbons, or: Liquefied gases
'Trioxygen difluoride': Various materials
See also LIQUEFIED NATURAL GAS

0466. Chloroformamidinium nitrate
[75524-40-2] **$CH_4ClN_3O_3$**



Alone, or Amines, or Metals

1. Sauermilch, W., *Explosivstoffe*, 1961, **9**, 71—74
2. Sorbe, 1968, 144

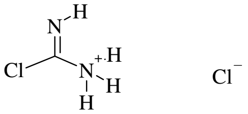
It is powerfully explosive, and also an oxidant which reacts violently with ammonia or amines, and causes explosive ignition of wet magnesium powder [1], or of powdered aluminium or iron [2].

See Chloroformamidinium chloride: Oxyacids, etc. (next below)

See other OXOSALTS OF NITROGENOUS BASES

0467. Chloroformamidinium chloride

[29671-92-9] **$CH_4Cl_2N_2$**



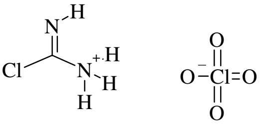
Oxyacids and salts

Sauermilch, W., *Explosivstoffe*, 1961, **9**, 71—74, 256

The title compound ('cyanamide dihydrochloride') reacts with perchloric acid to form the perchlorate salt, and with ammonium nitrate, the nitrate salt, both being highly explosive, and the latter also an oxidant.

0468. Chloroformamidinium perchlorate (Methanimidamide monoperchlorate)

[40985-41-9] **$CH_4Cl_2N_2O_4$**

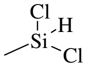


See item above

See other PERCHLORATE SALTS OF NITROGENOUS BASES

†0469. Dichloromethylsilane

[75-54-7] **CH_4Cl_2Si**



Oxidants

1. Müller, R. *et al., J. Prakt. Chem.*, 1966, **31**, 1—6
2. Sorbe, 1968, 128

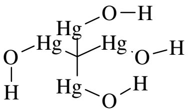
The pure material is not ignited by impact, but it is in presence of potassium permanganate or lead(II),(IV) oxide [1], or by copper oxide or silver oxide, even under an inert gas [2].

See Trichlorosilane

See other ALKYLHALOSILANES

0470. Tetrakis(hydroxymercurio)methane

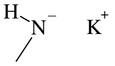
[ ] **$CH_4Hg_4O_4$**



Breitinger, D. K. *et al., Z. Naturforsch. B*, 1984, **39B**, 123

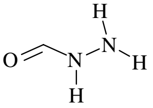
Intensive and heated high vacuum drying of the title compound (Hofmann's base) over phosphorus(V) oxide may lead to an explosion. Unheated drying appears satisfactory and safer.
See other MERCURY COMPOUNDS

0471. Potassium methylamide
[54448-39-4] (ion) **CH_4KN**



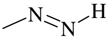
Makhija, R. C. *et al., Can. J. Chem.*, 1971, **49**, 807
Extremely hygroscopic and pyrophoric; may explode on contact with air.
See other *N*-METAL DERIVATIVES

0472. Formylhydrazine
[624-84-0] **CH_4N_2O**



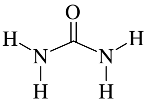
See 4-Amino-4H-1,2,4-triazole
See other HIGH-NITROGEN COMPOUNDS

0473. Methyldiazene
[26981-93-1] **CH_4N_2**



Oxygen
Ackermann, M. N. *et al., Inorg. Chem.*, 1972, **11**, 3077
Interaction on warming a mixture from —196°C rapidly to ambient temperature is explosive.
See related AZO COMPOUNDS

0474. Urea (Carbamide)
[57-13-6] **CH_4N_2O**



NSC 691, 1980; *HCS 1980*, 949

Chromyl chloride

See Chromyl chloride: Urea

Dichloromaleic anhydride, Sodium chloride

See Dichloromaleic anhydride: Sodium chloride, etc.

Metal hypochlorites

491M, 1975, 213

Urea reacts with sodium hypochlorite or calcium hypochlorite to form explosive nitrogen trichloride.

See Chlorine: Nitrogen compounds

Nitrosyl perchlorate

See Nitrosyl perchlorate: Organic materials

Oxalic acid

See Oxalic acid: Urea

Phosphorus pentachloride

See Phosphorus pentachloride: Urea

Preparative hazard for ^{15}N-labelled compound.

See Oxygen (Liquid): Ammonia, etc.

Sodium nitrite

See Sodium nitrite: Urea

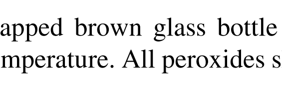
Titanium tetrachloride

See Titanium tetrachloride: Urea

See other ORGANIC BASES

0475a. Urea hydrogen peroxidate

[124-43-6] **$CH_4N_2O.H_2O_2$**



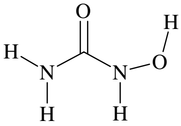
MCA Case History No. 719

The contents of a screw-capped brown glass bottle spontaneously erupted after 4 years' storage at ambient temperature. All peroxides should be kept in special storage and checked periodically.

See other CRYSTALLINE HYDROGEN PEROXIDATES, GLASS INCIDENTS

0475b. Hydroxyurea

[127-07-1] **$CH_4N_2O_2$**



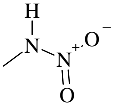
Cardillo, P. *et al., Chem. Eng. News*, 1998, **76**(22), 6

An industrial reactor containing a concentrate of this in water was left over the weekend, at an initial temperature possibly around 50°C. On the Tuesday morning it exploded. Investigation of the thermal stability of this drug in pure form showed it to be thermally unstable from 85°C as the solid, 70°C in aqueous solution. The decomposition is probably autocatalytic, gas evolving and with an enthalpy of 2.2 kJ/g. Aged samples were still less stable, decomposing after a variable induction period (from an initial 50°C, 80 hours). Gas evolution combined with temperature elevation to boiling point explains the burst reactor.

See other N—O COMPOUNDS

0476. *N*-Nitromethylamine

[598-57-2] **$CH_4N_2O_2$**



Diels, O. *et al., Berichte*, 1913, **46**, 2006.

A tiny quantity exploded with the utmost force when strongly heated in a capillary tube.

Amminemetals

Complexes with several ammine derivatives of metals are explosive.

See entry NITRAMINE—METAL COMPLEXES

Sulfuric acid

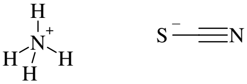
Urbanski, 1967, Vol. 3, 16

The nitroamine is decomposed explosively by conc. sulfuric acid.

See other *N*-NITRO COMPOUNDS

0477. Ammonium thiocyanate

[1762-95-4] **CH_4N_2S**



HCS 1980, 152

Other reactants

Yoshida, 1980, 227

MRH values calculated for 13 combinations, 12 with oxidants, are given.

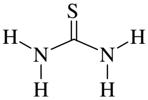
Potassium chlorate

See Potassium chlorate: Metal thiocyanates

See related CYANO COMPOUNDS

0478. Thiourea

[62-56-6] **CH_4N_2S**



Acrylaldehyde

See Acrylaldehyde: Acids, etc.

Hydrogen peroxide, Nitric acid

See Hydrogen peroxide: Nitric acid, etc.

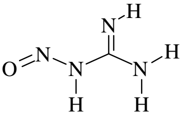
Potassium chlorate

See Potassium chlorate: Thiourea

See other ORGANIC BASES

0479. Nitrosoguanidine

[674-81-7] **CH_4N_4O**



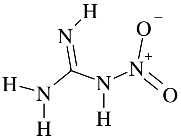
Henry, R. A. *et al., Ind. Eng. Chem.*, 1949, **41**, 846—849

The compound is normally stored and transported as a water-wet paste which slowly decomposes at elevated ambient temperatures, evolving nitrogen. Precautions are described to prevent pressure build-up in sealed containers.

See other NITROSO COMPOUNDS

0480. Nitroguanidine

[556-88-7] **$CH_4N_4O_2$**

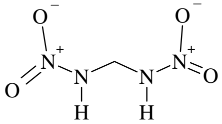


1. Urbanski, 1967, Vol. 3, 31
2. McKay, A. F., *Chem. Rev.*, 1952, **51**, 301

Nitroguanidine is difficult to detonate, but its mercury and silver complex salts are much more impact-sensitive [1]. Many nitroguanidine derivatives have been considered as explosives [2].

See other N—NITRO COMPOUNDS

0481. Methylenebis(nitramine)
[14168-44-6] **$CH_4N_4O_4$**

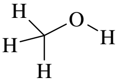


Glowiak, B., *Chem. Abs.*, 1960, **54**, 21761e

It is a powerful and sensitive explosive which explodes at 217°C, and the lead salt at 195°C.

See other N—NITRO COMPOUNDS

†0482. Methanol
[67-56-1] **CH_4O**



(*MCA SD-22*, 1970); *NSC 407*, 1979; *FPA H42*, 1975; *HCS 1980*, 628; *RSC Lab. Hazard Data Sheet No. 25*, 1984

Ferris, T. V., *Loss Prev.*, 1974, **8**, 15—19

Explosive behaviour on combustion of methanol—air mixtures at 1.8 bar and 120°C was studied, with or without addition of oxygen and water.

Acetyl bromide

See Acetyl bromide: Hydroxylic compounds

Alkylaluminium solutions

MCA Case History No. 1778

Accidental use of methanol in place of hexane to rinse out a hypodermic syringe used for a dilute alkylaluminium solution caused a violent reaction which blew the plunger out of the barrel.

See ALKYLALUMINIUM DERIVATIVES: Alcohols

Beryllium hydride

See Beryllium hydride: Methanol

Boron trichloride

See Boron trichloride

Carbon tetrachloride, Metals

Kuppers, J. R., *J. Electrochem. Soc.*, 1978, **125**, 97—98

The rapid autocatalytic dissolution of aluminium, magnesium or zinc in 9:1 methanol—carbon tetrachloride mixtures is sufficiently vigorous to be rated as potentially hazardous. Dissolution of zinc powder is subject to an induction period of 2 h, which is eliminated by traces of copper(II) chloride, mercury(II) chloride or chromium(III) bromide.

See other INDUCTION PERIOD INCIDENTS

Chloroform, Sodium

See Chloroform: Sodium, Methanol

Chloroform, Sodium hydroxide

See Chloroform: Sodium hydroxide, Methanol

Cyanuric chloride

See 2,4,6-Trichloro-1,3,5-triazine: Methanol

Dichloromethane

See Dichloromethane: Air, etc.

Diethylzinc

See Diethylzinc: Methanol

Hydrogen peroxide, sulfur trioxide

See Hydrogen peroxide, Methanol, Sulfur trioxide

Hydrogen, Raney nickel catalyst

Klais, O., *Hazards from Pressure, IChE Symp. Ser. No. 102*, 25—36, Oxford, Pergamon, 1987

During hydrogenation of an unspecified substrate in methanol solution under hydrogen at 100 bar with Raney nickel catalyst, a sudden temperature increase led to hydrogenolysis of methanol to methane, and the pressure increase led to an overpressure accident. Such incidents may be avoided by control of agitation, limiting the amount of catalyst, and checking thermal stability of starting materials and end products beforehand.

See other GAS EVOLUTION INCIDENTS

Metals

See Aluminium: Methanol
Magnesium: Methanol
Potassium (Slow oxidation)

Other reactants

Yoshida, 1980, 360

MRH values calculated for 17 combinations, largely with oxidants, are given.

Oxidants MRH values show % of oxidant

See Barium perchlorate: Alcohols
Bromine: Alcohols
Chlorine: Methanol

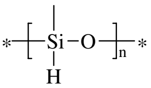
Chromium trioxide: Alcohols
Hydrogen peroxide: Oxygenated compounds MRH 5.98/76
Lead perchlorate: Methanol
Nitric acid: Alcohols (reference 6) MRH 5.31/70
Sodium hypochlorite: Methanol MRH 2.47/90

Phosphorus(III) oxide
See Tetraphosphorus hexaoxide: Organic liquids

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

Water
MCA Case History Nos. 1822, 2085
Static discharge ignited the contents of a polythene bottle being filled with a 40:60 mixture of methanol and water at 30°C, and a later similar incident in a plastics-lined metal tank involved a 30:70 mixture.

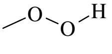
0483. Poly[oxy(methyl)silylene]
[9004-73-3] **$(CH_4OSi)_n$**



1-Allyloxy-2,3-epoxypropane
Anon., *Eur. Chem. News*, 1995, **63**(1656), 27
The two compounds were accidentally mixed in a reactor because of similar packaging. They reacted uncontrollably, rupturing the reactor, and the evolved hydrogen ignited, killing one worker and injuring four. If as is probable a base catalyst was present depolymerisation/disproportionation to oxomethylsilane and methylsilane is also possible, with an increase in both vapour pressure and flammability.
See other SILANES

Preparative hazard
Crivello, J. V. *et al., Chem. Abs.*, 1990, **113**, 41011z; U.S. Pat. 4,895,967.
A procedure for cyclisation of the linear polymer to small oligomers without risk of explosion is described.

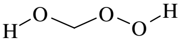
0484. Methyl hydroperoxide
[3031-73-0] **CH_4O_2**



Alone, or Phosphorus(V) oxide, or Platinum
1. Rieche, A. *et al., Ber.*, 1929, **62**, 2458, 2460
2. Hasegawa, K. *et al., Proc. Int. Pyrotech. Semin.*, 1994, (19th), 684

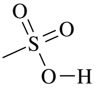
The hydroperoxide is violently explosive and shock-sensitive, especially on warming; great care is necessary in handling. It explodes violently in contact with phosphorus pentaoxide, and a 50% aqueous solution decomposed explosively on warming with spongy platinum [1]. The barium salt is dangerously explosive when dry [2].
See other ALKYL HYDROPEROXIDES

0485. Hydroxymethyl hydroperoxide
[15932-89-5] **CH_4O_3**



Rieche, A., *Ber.*, 1931, **64**, 2328; 1935, **68**, 1465
It explodes on heating, but is friction-insensitive. Higher homologues are not explosive.
See other 1-OXYPEROXY COMPOUNDS

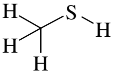
0486. Methanesulfonic acid
[75-75-2] **CH_4O_3S**



Ethyl vinyl ether
See Ethyl vinyl ether: Methanesulfonic acid

Hydrogen fluoride
See Hydrogen fluoride: Methanesulfonic acid
See other ORGANIC ACIDS

†0487. Methanethiol
[74-93-1] **CH_4S**



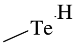
FPA H93, 1980; *HCS 1980*, 655

Chlorine
See Chlorine: Methanethiol

Mercury(II) oxide
See Mercury(II) oxide: Methanethiol
See other ALKANETHIOLS, ALKYLNON-METAL HYDRIDES

0488. Methanetellurol

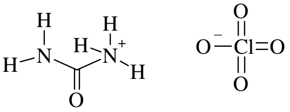
[25284-83-7] **CH_4Te**



Hamada, K. *et al., Synth. React. Inorg. Metal-Org. Chem.*, 1977, **7**, 364 (footnote 1)
It ignites in air and explodes with oxygen at ambient temperature.
See other ALKYLNON-METAL HYDRIDES

0489. Uronium perchlorate (Urea perchlorate)

[18727-07-6] **$CH_5ClN_2O_5$**



Aromatic nitro compounds

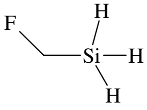
1. Shimio, K. *et al., Chem. Abs.*, 1975, **83**, 134504
2. Fujiwara, S. *et al.*, Japan Kokai, 74 134 812, 1974

Conc. aqueous solutions of the urea salt will dissolve solid or liquid aromatic nitro compounds (e.g. picric acid [1], or nitrobenzene [2]) to give high velocity explosives.
See next item below

Organic materials
Kusakabe, M. *et al., Chem. Abs.*, 1980, **92**, 79028
Liquid mixtures with detonable materials (picric acid, nitromethane) were extremely powerful explosives, and those with nitrobenzene or dimethylformamide less so.
See other PERCHLORATE SALTS OF NITROGENOUS BASES

0490. Fluoromethylsilane

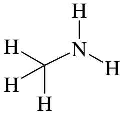
[10112-08-0] **CH_5FSi**



Chlorine, Dichloromethane
See Chlorine: Fluoromethylsilane, Dichloromethane
See other SILANES: halogens

†0491. Methylamine (Methanamine)

[74-89-5] **CH_5N**



(*MCA SD-57*, 1965); *HCS 1980*, 637

Nitromethane

See Nitromethane: Acids, etc.

Other reactants

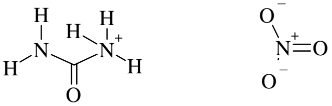
Yoshida, 1980, 362

MRH values calculated for 13 combinations with oxidants are given.

See other ORGANIC BASES

0492. Uronium nitrate (Urea nitrate)

[124-47-0] **$CH_5N_3O_4$**



1. Kirk-Othmer, 1970, Vol. 21, 38
2. Markalous, F. *et al.*, Czech Pat. 152 080, 1974
3. Lazarov, S. *et al., Chem. Abs.*, 1973, **79**, 94169
4. Medard, L., *Mém. Poudres*, 1951, **33**, 113—123

(English transl. HSE 11292 available from HSE/LIS, 1986)

The nitrate decomposes explosively when heated [1]. Prepared in the presence of phosphates, the salt is much more stable, even when dry [2]. The manufacture and explosive properties of urea nitrate and its mixtures with other explosives are discussed in detail [3]. Explosive properties of the nitrate are detailed [4].

Heavy metals

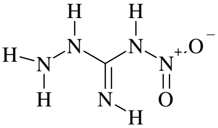
Kotzerke, *Proc. 1st Int. Symp. Prev. Occ. Risks Chem. Ind.*, 201—207, Heidelberg, ISSA, 1970

During evaporation of an alkaline aqueous solution of the nitrate, decomposition led to gas evolution and a pressure explosion occurred. This was attributed to the use of recovered alkali containing high levels of lead and iron, which were found to catalyse the thermal decomposition of the nitrate. Precautions to prevent recurrence are detailed.

See other GAS EVOLUTION INCIDENTS, OXOSALTS OF NITROGENOUS BASES

0493. 1-Amino-3-nitroguanidine

[18264-75-0] **$CH_5N_5O_2$**



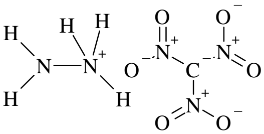
Lieber, E. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 2328

It explodes at the m.p., 190°C.

See other HIGH-NITROGEN COMPOUNDS, N—NITRO COMPOUNDS

0494a. Hydrazinium trinitromethanide (Hydrazinium nitroformate)

[14913-74-7] **$CH_5N_5O_6$**



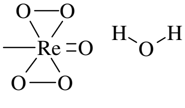
1. Anan, T. *et al, Chem. Abs.*, 1995, **123**, 174351
2. Schoyer, H. F. R. *et al., J. Propul. Power.*, 1995, **11**(4), 856
3. van Zelst, M. *et al., Chem. Abs.*, 2000, **133**, 283725

The compound was examined as a propellant explosive, it proved easily detonable and more sensitive than ammonium perchlorate. A formulation with hydroxyl terminated polybutadiene binder ignited spontaneously at room temperature [1]. Other workers have found it more tractable [2]. Detailed study of properties has been made. It is too friction sensitive for safe transport [3].

See other HYDRAZINIUM SALTS, POLYNITROALKYL COMPOUNDS

0494b. Methylbis(η^2-peroxo)rhenium oxide hydrate

[ ] **CH_5O_6Re**



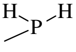
Herrmann, W. A. *et al., Angew. Chem. (Int.)*, 1993, **32**, 1157

This, the active species in methylrheniumtrioxide catalysed peroxidations by hydrogen peroxide, is fairly stable in solution but explosive when isolated.

See other ORGANOMETALLIC PEROXIDES

0495. Methylphosphine

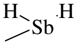
[593l-54-4] **CH_5P**



Houben-Weyl, 1963, Vol. 12.1, 69
Primary lower-alkylphosphines readily ignite in air.
See other ALKYLPHOSPHINES

0496. Methylstibine

[23362-09-6] **CH_5Sb**



Sorbe, 1968, 28
Alkylstibines decompose explosively on heating or shock.
See other ALKYLMETAL HYDRIDES

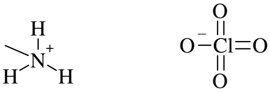
0497. Methylammonium chlorite

[15875-44-2] **CH_6ClNO_2**

Levi, G. R., *Gazz. Chim. Ital. [1]*, 1922, **52**, 207
A conc. solution caused a slight explosion when poured onto a cold iron plate.
See other CHLORITE SALTS, OXOSALTS OF NITROGENOUS BASES

0498. Methylammonium perchlorate

[15875-44-2] **CH_6ClNO_4**

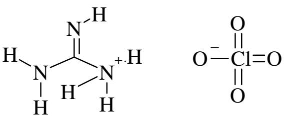


1. Kasper, F., *Z. Chem.*, 1969, **9**, 34
2. Kempson, R. M., *Chem. Abs.*, 1980, **92**, 61259

The semi-crystalline mass exploded when stirred after standing overnight. The preparation was based on a published method used uneventfully for preparation of ammonium, dimethylammonium and piperidinium perchlorates [1]. Its use in explosives and propellants has been surveyed [2].
See other PERCHLORATE SALTS OF NITROGENOUS BASES

0499. Guanidinium perchlorate

[10308-84-6] **$CH_6ClN_3O_4$**



1. Davis, 1943, 121
2. Schumacher, 1960, 213
3. Fujiwara, S. *et al., Chem. Abs.*, 1980, **92**, 200443
4. Udupa, M. R., *Propellants, Explos., Pyrotech.*, 1983, **8**, 109—111

Unusually sensitive to initiation and of high explosive power [1], it decomposes violently at 350°C [2]. The explosive properties have been determined [3], and thermal decomposition at 275—325° was studied in detail [4].

See DIFFERENTIAL THERMAL ANALYSIS (reference 1)

Iron(III) oxide

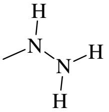
Isaev, R. N. *et al., Chem. Abs.*, 1970, **73**, 132626

Addition of 10% of iron oxide reduces the thermal stability of the salt.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

†0500. Methylhydrazine

[60-34-4] **CH_6N_2**



491M 1975, 259

When extensively exposed to air (as a thin film, or absorbed on fibrous or porous solids), it may ignite.

Dicyanofurazan

See Dicyanofurazan: Nitrogenous bases

Oxidants

Kirk-Othmer, 1966, Vol. 11, 186

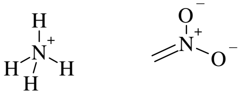
A powerful reducing agent and fuel, hypergolic with many oxidants such as dinitrogen tetraoxide or hydrogen peroxide.

See ROCKET PROPELLANTS

See other ORGANIC BASES, REDUCANTS

0501. Ammonium *aci*-nitromethanide

[ ] **$CH_6N_2O_2$**



Watts, C. E., *Chem. Eng. News*, 1952, **30**, 2344

The isolated salt is a friction-sensitive explosive.

See other aci-NITRO SALTS

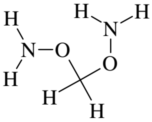
0502a. Methylammonium nitrite
[68897-47-2] **$CH_6N_2O_2$**

Hara, Y., *Chem. Abs.*, 1982, **97**, 55056

It is unstable at ambient temperature, and is formed on contact of the nitrate with sodium or potassium nitrites.

See other NITRITE SALTS OF NITROGENOUS BASES, OXOSALTS OF NITROGENOUS BASES

0502b. Methylenebis(oxyamine)
$CH_6N_2O_2$



Tollison, K. *et al., J. Energetic Mat.,* 2001, **19**(4), 277

Salts of this diamine (which probably does not exist as free base) with nitric and perchloric acids, dinitramine and trinitromethane were prepared, they were isolable, but far too unstable to consider as propellant explosive components. Many were too sensitive to consider handling on large scale.

HYDROXYLAMINIUM SALTS

0503. Methylammonium nitrate (Methanaminium nitrate)
[1941-24-8] **$CH_6N_2O_3$**

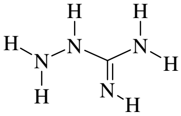
1. Biasutti, 1981, 145
2. Miron, Y., J. *Haz. Mat.*, 1980, **3**, 301—321
3. Hara, Y., *Chem. Abs.*, 1982, **97**, 55056

Rail tanks of 86% aqueous solutions or slurries of the salt exploded, apparently during pump-transfer operations [1]. The course and mechanism or thermal decomposition has been investigated. Traces of rust or copper powder catalyse and accelerate the decomposition, so corrosion prevention is an important aspect of safety measures [2]. It is of higher thermal stability than the chlorate salt, or the nitrite, which decomposes at ambient temperature [3].

See other CATALYTIC IMPURITY INCIDENTS, OXOSALTS OF NITROGENOUS BASES

0504. Aminoguanidine

[79-17-4] **CH_6N_4**



Kurzer, F. *et al., Chem. & Ind.*, 1962, 1585

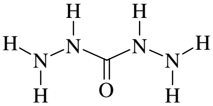
All the oxoacid salts are potentially explosive, including the wet nitrate.

See Aminoguanidinium nitrate

See other HIGH-NITROGEN COMPOUNDS, ORGANIC BASES

0505. Carbonic dihydrazide

[497-18-7] **CH_6N_4O**



Sorbe, 1968, 74

It explodes on heating.

Nitrous acid

Curtius, J. *et al., Ber.*, 1894, **27**, 55

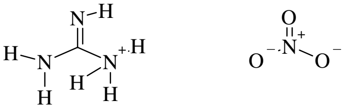
Interaction forms the highly explosive carbonic diazide.

See Carbonic diazide

See other HIGH-NITROGEN COMPOUNDS

0506. Guanidinium nitrate

[52470-25-4] **$CH_6N_4O_3$**



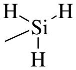
1. Davis, T. L., *Org. Synth.*, 1944, Coll. Vol. 1, 302
2. Smith, G. B. L., and Schmidt, M. T., *Inorg. Synth.*, 1939, **1**, 96, 97
3. Schopf, C. *et al., Angew. Chem.*, 1936, **49**, 23
4. Udupa, M. R., *Thermochim. Acta*, 1982, **53**, 383—385
5. Medard, L. *Mém. Poudres*, 1951, **33**, 113—123 (English transl. HSE 11292 available from HSE/LIS, 1986)
6. Indian Pat. IN 157 293, Projects and Developments (India) Ltd., 1986 (*Chem. Abs.*, 1986, **105**, 210788)

According to an O.S. amendment sheet, the procedure as described [1] is dangerous because the reaction mixture (dicyanodiamide and ammonium nitrate) is similar in composition to commercial blasting explosives. This probably also applies to similar earlier preparations [2]. An earlier procedure which involved heating ammonium thiocyanate, lead nitrate and ammonia demolished a 50 bar autoclave [3]. TGA and DTA studies show that air is not involved in the thermal decomposition [4]. Explosive properties of the nitrate are detailed [5]. An improved process involves catalytic conversion at 90—200°C of a molten mixture of urea and ammonium nitrate to give 92% conversion (on urea) of guanidinium nitrate, recovered by crystallisation. Hazards of alternative processes are listed [6].

See other OXOSALTS OF NITROGENOUS BASES

0507. Methylsilane

[992-94-9] **CH_6Si**



Mercury, Oxygen

Stock, A. *et al., Ber.*, 1919, **52**, 706

It does not ignite in air, but explodes if shaken with mercury in oxygen.

See other ALKYLSILANES

0508. Methylhydrazinium nitrate

[29674-96-2] **$CH_7N_3O_3$**

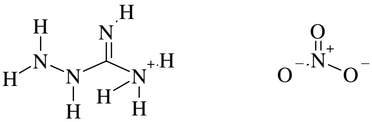
Lawton, E. A. *et al., J. Chem. Eng. Data*, 1984, **29**, 358

Impact sensitivity is comparable to that of ammonium perchlorate.

See other OXOSALTS OF NITROGENOUS BASES

0509. Aminoguanidinium nitrate

[10308-82-4] **$CH_7N_5O_3$**



Koopman, H., *Chem. Weekbl.*, 1957, **53**, 97

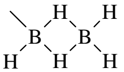
An aqueous solution exploded violently during evaporation on a steam bath. Nitrate salts of many organic bases are unstable and should be avoided.

See Aminoguanidine

See other HIGH-NITROGEN COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

0510. Methyldiborane

[23777-55-1] **CH_8B_2**



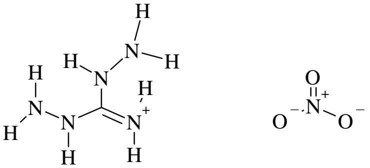
Bunting, *Inorg. Synth.*, 1979, 19, 237

It ignites explosively in air.

See other ALKYLBORANES

0511. Diaminoguanidinium nitrate

[10308-83-5] **$CH_8N_6O_3$**



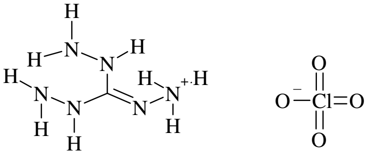
Violent decomposition at 260°C.

See entry DIFFERENTIAL THERMAL ANALYSIS (reference 1)

See other OXOSALTS OF NITROGENOUS BASES

0512. Triaminoguanidinium perchlorate

[4104-85-2] **$CH_9ClN_6O_4$**



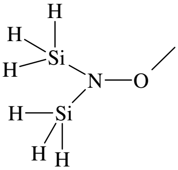
Violent decomposition at 317°C.

See entry DIFFERENTIAL THERMAL ANALYSIS (reference 1)

See other PERCHLORATE SALTS OF NITROGENOUS BASES

0513. *O*-Methyl-*N,N*-disilylhydroxylamine

[ ] **CH_9NOSi_2**



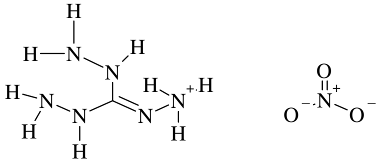
Mitzel, N. W. *et al., J. Amer. Chem. Soc.*, 1996, **118**(11), 2664

Reasonably stable at ambient temperature, the compound explodes if heated to 200°C

See other N—O COMPOUNDS, SILANES

0514. Triaminoguanidinium nitrate

[4000-16-2] **$CH_9N_7O_3$**



Violent decomposition at 230°C.

See entry DIFFERENTIAL THERMAL ANALYSIS (reference 1)

See other OXOSALTS OF NITROGENOUS BASES

0515. Caesium cyanotridecahydrodecaborate(2—)

[71250-00-5] **$CH_{13}B_{10}Cs_2N$**

$Cs_2[B_{10}H_{13}C{\equiv}N]$

Hydrochloric acid

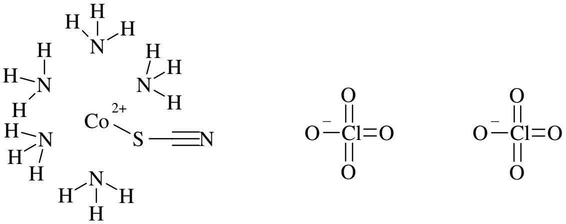
Schultz, R. V. *et al., Inorg. Chem.*, 1979, **18**, 2883

Addition of the salt to conc. hydrochloric acid is extremely exothermic.

See other CYANO COMPOUNDS

0516. Pentaamminethiocyanatocobalt(III) perchlorate

[15663-42-0] **$CH_{15}Cl_2CoN_6O_8S$**

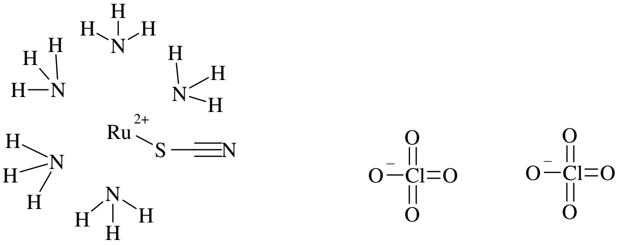


Explodes at 325°C; medium impact-sensitivity.

See entry AMMINEMETAL OXOSALTS (reference 3)

0517. Pentaamminethiocyanatoruthenium(III) perchlorate

[38139-15-0] **$CH_{15}Cl_2N_6O_8RuS$**



Armour, J. N., private comm., 1969

After washing with ether, 0.1 g of the complex exploded violently when touched with a spatula.

See other AMMINEMETAL OXOSALTS, REDOX COMPOUNDS

0518. Hafnium carbide

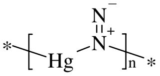
[12069-85-1] **CHf**

$Hf^{4+} \quad C^{4-}$

See entry REFRACTORY POWDERS

0519. Poly(diazomethylenemercury) ('Mercury diazocarbide')

[31724-50-2] **$(CHgN_2)_n$**



Houben-Weyl, 1974, Vol. 13.2b, 19

Interaction of diazomethane with bis(trimethylsilylamino)mercury gives the polymeric explosive solid.

See other DIAZO COMPOUNDS, MERCURY COMPOUNDS

0520. Mercury(I) cyanamide

[72044-13-4] **CHg_2N_2**

$Hg^{+}{-}Hg^{+} \quad N^{2-}{\equiv}N$

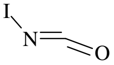
Deb, S. K. *et al., Trans. Faraday Soc.*, 1959, **55**, 106—113

Relatively large particles explode on heating rapidly to 325°C, or under high-intensity illumination when confined.

See other IRRADIATION DECOMPOSITION INCIDENTS, MERCURY COMPOUNDS, *N*-METAL DERIVATIVES

0521. Iodine isocyanate

[3607-48-5] **CINO**



Rosen, S. *et al., Anal. Chem.*, 1966, **38**, 1394

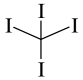
On storage, solutions of iodine isocyanate gradually deposit a touch-sensitive, mildly explosive solid (possibly cyanogen peroxide).

See other IODINE COMPOUNDS

See related N-HALOGEN COMPOUNDS

0522. Carbon tetraiodide (Tetraiodomethane)

[507-25-5] **CI_4**



Bromine trifluoride

See Bromine trifluoride: Halogens, etc.

Lithium

See Lithium: Halocarbons

See other HALOALKANES

0523. Potassium cyanide

[151-50-8] **CKN**

HCS 1980, 764

Mercury(II) nitrate

See Mercury(II) nitrate: Potassium cyanide

Nitrogen trichloride

See Nitrogen trichloride: Initiators

Perchloryl fluoride

See Perchloryl fluoride: Calcium acetylide, etc.

Sodium nitrite

See Sodium nitrite: Metal cyanides

See entry METAL CYANIDES (AND CYANO COMPLEXES) (reference 1)

0524. Potassium cyanide—potassium nitrite

[ ] **$CKN.KNO_2$**

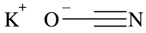
Sorbe, 1968, 68

The double salt (a redox compound) is explosive.

See other REDOX COMPOUNDS

0525. Potassium cyanate

[590-28-3] **CKNO**



Water

Prinsky, M. L. *et al., J. Loss Prev. Process Ind.*, 1990, **3**, 345

A drum of 30% solution in water exploded an hour after filling at 50°C, despite having a vent. Calorimetry demonstrated an exothermic, autocatalytic hydrolysis to ammoniacal potassium bicarbonate. In theory, a pressure exceeding 30 bar is obtainable. Aqueous solutions are unstable even at room temperature. Similar hydrolysis may account for an explosive product with Gold(III) chloride.

See Gold(III) chloride

See related METAL CYANATES, METAL CYANIDES

0526. Potassium thiocyanate

[333-20-0] **CKNS**

HCS 1980, 778

Calcium chlorite

See Calcium chlorite: Potassium thiocyanate

Other reactants

Yoshida, 1980, 228

MRH values calculated for 13 combinations with oxidants are given.

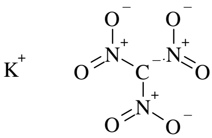
Perchloryl fluoride

See Perchloryl fluoride: Calcium acetylide, etc.

See related METAL CYANIDES

0527. Potassium trinitromethanide

[14268-23-6] **CKN_3O_6**



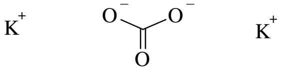
1. Sandler, S. R. *et al., Organic Functional Group Preparations*, 433, New York, Wiley, 1968
2. Shulgin, A. T., private comm., 1968

This intermediate, produced by action of alkali on tetranitromethane, must be kept damp and used as soon as possible with great care, as it may be explosive [1]. Material produced as a by-product in a nitration reaction using tetranitromethane was washed with acetone. It exploded very violently after several months' storage [2].

See other POLYNITROALKYL COMPOUNDS

0528. Potassium carbonate

[584-08-7] **CK_2O_3**



Carbon

Druce, J. G. F., *School Sci. Rev.*, 1926, **7**(28), 261

Potassium metal prepared by the old process of distilling an intimate mixture of the carbonate and carbon contained some 'carbonylpotassium' (actually potassium benzenehexoxide), and several explosions with old samples of potassium may have involved this compound (or, perhaps more likely, potassium superoxide).

See Potassium (Slow oxidation)

Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Magnesium

See Magnesium: Potassium carbonate

See other INORGANIC BASES, METAL OXONON-METALLATES

0529. Lithium thiocyanate

[556-65-0] **CLiNS**

1,3-Dioxolane

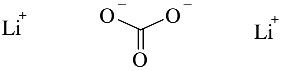
Rao, B. L. M. *et al., J. Electrochem. Soc.*, 1980, **127**, 2333—2335

Thermal decomposition of the thiocyanate in air at 650°C yields 0.01% of volatile cyanide, but presence of moisture or the solvent increases cyanide evolution to 0.5—1.5 wt%.

See related METAL CYANIDES

0530. Lithium carbonate

[554-13-2] **CLi_2O_3**



HCS 1980, 594

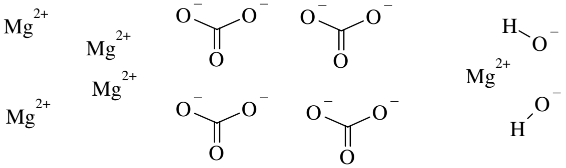
Fluorine

See Fluorine: Metal salts

See other INORGANIC BASES, METAL OXONON-METALLATES

0531. Magnesium carbonate hydroxide

[39409-82-0] **$CMgO_3.\frac{1}{4}H_2MgO_2$**



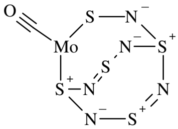
Formaldehyde

See Formaldehyde: Magnesium carbonate hydroxide

See other INORGANIC BASES, METAL OXONON-METALLATES

0532. Carbonyl(pentasulfur pentanitrido)molybdenum

[ ] **$CMoN_5OS_5$**



Wynne, K. J. *et al., J. Inorg. Nucl. Chem.*, 1968, **30**, 2853

A shock- and heat-sensitive amorphous compound of uncertain structure. A sample exploded violently when scraped from a glass sinter, under impact from a hammer, on sudden heating to 260°C or when added to conc. sulfuric acid.

See related CARBONYLMETALS, N—S COMPOUNDS

0533. Sodium cyanide

[143-33-9] **CNNa**

$Na^+ \ \bar{C}\equiv N$

HCS 1980, 836, 837 (30% solution)

Benzyl chloride

See Benzyl chloride: Methanol, Sodium cyanide, etc.

Ethyl chloroacetate

See Ethyl chloroacetate: Sodium cyanide

Oxidants

See entry METAL CYANIDES (AND CYANO COMPLEXES) (reference 1)

0534. Sodium fulminate

[15736-98-8] **CNNaO**

$$Na^{+} \quad \overset{-}{C}{\equiv}\overset{+}{N}{-}O^{-}$$

Smith, 1966, Vol. 2, 99

Even sodium fulminate detonates when touched lightly with a glass rod.

See other METAL FULMINATES

0535. Sodium thiocyanate

[540-72-7] **CNNaS**

$$Na^{+} \qquad S^{-}{-}{\equiv}N$$

Other reactants

Yoshida, 1980, 229

MRH values calculated for 14 combinations with a variety of reagents are given.

Sodium nitrate

See Sodium nitrate: Sodium thiocyanate

Sodium nitrite MRH 3.51/72

See Sodium nitrite: Sodium thiocyanate

Sulfuric acid

See Sulfuric acid: Sodium thiocyanate

See related METAL CYANIDES

0536. Thallium fulminate

[20991-79-1] **CNOTl**

$$Tl^{+} \quad \overset{-}{C}{\equiv}\overset{+}{N}{-}O^{-}$$

Boddington, T. *et al., Trans. Faraday Soc.*, 1969, **65**, 509

Explosive, even more shock- and heat-sensitive than mercury(I) fulminate.

See other METAL FULMINATES

0537. Cyanonitrene

[1884-64-6] **CN_2**

$$N{\equiv}{-}N{:}$$

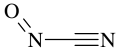
Hutchins, M. G. K. *et al., Tetrahedron Lett.*, 1981, **22**, 4599—4602

Interaction of sodium hydrogen cyanamide and *tert*-butyl hypochlorite in methanol at —50°C to ambient temperature forms cyanonitrene. Isolation gave an orange dimeric residue which exploded on two occasions.

See related CYANO COMPOUNDS

0538. Nitrosyl cyanide

[4343-68-4] **CN_2O**



Alone, or Nitrogen oxide

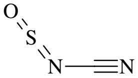
1. Kirby, G. W., *Chem. Soc. Rev.*, 1977, 9
2. Keary, C. M. *et al., J. Chem. Soc., Perkin Trans. 2*, 1978, 243

Direct preparation of the gas is potentially hazardous, and explosive decomposition of the impure gas in the condensed state (below —20°C) has occurred. A safe procedure involving isolation of the 1:1 adduct with 9,10-dimethylanthracene is preferred. The impure gas contains nitrogen oxide and it is known that nitrosyl cyanide will react with the latter to form an explosive compound [1]. The need to handle this compound of high explosion risk in small quantities, avoiding condensed states, is stressed [2].

See other CYANO COMPOUNDS, NITROSO COMPOUNDS

0539. Sulfinylcyanamide

[16342-87-3] **CN_2OS**



Alone, or Ethanol, or Water

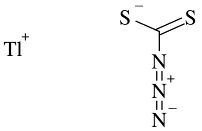
Scherer, O. J. *et al., Angew. Chem. (Intern. Ed.)*, 1967, **6**, 701—702

The crude highly unsaturated material decomposes explosively if stored in a refrigerator or on attempted distillation under water-pump vacuum (moisture?). However, it is distillable under oil-pump vacuum and is then stable in refrigerated storage. It decomposes explosively with traces of water or ethanol, and polymerises in daylight at ambient temperature.

See other CYANO COMPOUNDS, N—S COMPOUNDS

0540. Thallium(I) azidodithiocarbonate (Thallium(I) dithiocarbonazidate)

[ ] **CN_3S_2Tl**



Sulfuric acid

Bailar, 1973, Vol. 1, 1155

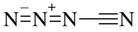
The highly unstable explosive salt is initiated by contact with sulfuric acid.

See Azidodithioformic acid

See related ACYL AZIDES

0541. Cyanogen azide

[764-05-6] **CN_4**



1. Marsh, F. D., *J. Amer. Chem. Soc.*, 1964, **86**, 4506
2. Marsh, F. D., *J. Org. Chem.*, 1972, **37**, 2966
3. Coppolino, A. P., *Chem. Eng. News*, 1974, **52**(25), 3
4. Mardell, L., *Chem. in Brit.*, 1995, **31**(8), 591

It detonates with great violence when subjected to mild mechanical, thermal or electrical shock [1]. Special precautions are necessary to prevent separation of the azide from solution and to decontaminate equipment and materials [2]. The azide is not safe in storage at —20°C as previously stated. A sample exploded immediately after removal from refrigerated (dark) storage [3]. A student was performing a preparation involving in situ generation of cyanogen azide in acetonitrile. Some unexpected white needles crystallised from the mixture, were filtered, dried on the filter (probably a glass sinter) and scraped off, this caused an explosion removing the student's thumb. It is hypothesised that water contamination, or excess sodium azide, had induced formation of diazidomethylenecyanamide or sodium 5-azidotetrazolide, which had crystallised [4].

See Diazidomethylenecyanamide

Sodium hydroxide

Marsh, F. D., *J. Org. Chem.*, 1972, **37**, 2966

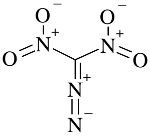
Interaction with 10% alkali forms sodium 5-azidotetrazolide, which is violently explosive if isolated.

See 5-Azidotetrazole

See related HALOGEN AZIDES

0542. Dinitrodiazomethane

[25240-93-1] **CN_4O_4**



Alone, or Sulfuric acid

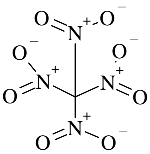
Schallkopf, V. *et al., Angew. Chem. (Intern. Ed.)*, 1969, **8**, 612

It explodes on impact, rapid heating or contact with sulfuric acid.

See other DIAZO COMPOUNDS, POLYNITROALKYL COMPOUNDS

0543. Tetranitromethane

[509-14-8] **CN_4O_8**



1. Liang, P., *Org. Synth.*, 1955, Coll. Vol. 3, 804
2. *MCA Guide*, 1972, 310 (reference 9)

During its preparation from fuming nitric acid and acetic anhydride, strict temperature control and rate of addition of anhydride are essential to prevent a runaway violent reaction [1]. An explosion occurred during preparation in a steel tank [2]. It should not be distilled, as explosive decomposition may occur [1].
See Nitric acid: Acetic anhydride

Aluminium
See Aluminium: Oxidants

Amines
Gol'binder, A. A., *Chem. Abs.*, 1963, **59**, 9730b
Mixtures of amines, for example aniline, with tetranitromethane (19.5%) ignite in 35—55 s, and will proceed to detonation if the depth of liquid is above a critical value.

Aromatic nitro compounds

1. Urbanski, 1964, Vol. 1, 592
2. Zotov, E. V. *et al., Chem. Abs.*, 1982, **98**, 5965

Mixtures with nitrobenzene, 1- or 4-nitrotoluene, 1,3-dinitrobenzene or 1-nitronaphthalene were found to be high explosives of high sensitivity and detonation velocities [1]. Those with nitrobenzene are spark-detonable [2].

Dienes
Eberson, L. *et al., Acta Chem. Scand.*, 1998, **52**(4), 450
Tetranitromethane adds across various non-conjugated dienes to give cyclic products. The products with norbornadiene and cycloocta-1,5-diene are subject to spontaneous violent decomposition.

Ferrocene
Jaworska-Augustyniak, A., *Transition Met. Chem.*, 1979, **4**, 207—208
Contact of tetranitromethane with ferrocene under various conditions leads to violent explosions, though not if the latter is dissolved in methanol or cyclohexane. Other ferrocene derivatives react violently, but not the dimethyl compound.

Hydrocarbons

1. Stettbacher, A., *Z. Ges. Schiess. Sprengstoffw.*, 1930, **25**, 439
2. Hager, K. F., *Ind. Eng. Chem.*, 1949, **41**, 2168
3. Tschinkel, J. G., *Ind. Eng. Chem.*, 1956, **48**, 732
4. Stettbacher, A., *Tech. Ind. Schweiz. Chem. Ztg.*, 1941, **24**, 265—271
5. Anon., *Chem. Ztg.*, 1920, **44**, 497
6. Zotov, E. V. *et al,., Chem. Abs.*, 1980, **93**, 49732, 49734

When mixed with hydrocarbons in approximately stoicheiometric proportions, a sensitive highly explosive mixture is produced which needs careful handling [1][2]. The use of such mixtures as rocket propellants has also been investigated [3]. Explosion of only 10 g of a mixture with toluene caused 10 deaths and 20 severe injuries [4]. The mixture contained excess toluene in error [5]. Detonation characteristics of mixtures with benzene, toluene (and nitrobenzene) were studied [6].

Pyridine

Isaacs, N. S. *et al., Tetrahedron Lett.*, 1982, **23**, 2802

Mixtures occasionally have exploded several hours after preparation.

Sodium ethoxide

Macbeth, A. K., *Ber.*, 1913, **46**, 2537—2538

Addition of the last of several portions of the ethoxide solution caused the violent explosion of 30 g of tetranitromethane (possibly involving formation of sodium trinitromethanide).

See Potassium trinitromethanide

Toluene, Cotton

Winderlich, R., *J. Chem. Educ.*, 1950, **27**, 669

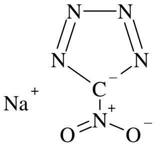
A demonstration mixture, to show combustion of cellulose by combined oxygen, exploded with great violence soon after ignition.

See Hydrocarbons, above

See other OXIDANTS, POLYNITROALKYL COMPOUNDS

0544. Sodium 5-nitrotetrazolide

[67312-43-0] **CN_5NaO_2**



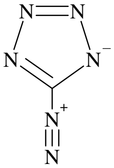
1. Spear, R. J., *Aust. J. Chem.*, 1982, **35**, 10
2. Redman, L. D. *et al., Chem. Abs.*, 1984, **100**, 194540

Extremely sensitive to mechanical initiation, it should be treated as a primary explosive [1]. A batch of the dihydrate exploded spontaneously [2].

See other *C*-NITRO COMPOUNDS, TETRAZOLES

0545. 5-Diazoniotetrazolide

[13101-58-1] **CN_6**



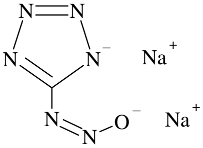
Thiele, J., *Ann.*, 1892, **270**, 60

Conc. aqueous solutions of this internal diazonium salt explode at 0°C.

See other DIAZONIUM SALTS, TETRAZOLES

0546. Disodium tetrazole-5-diazoate

[ ] **CN_6Na_2O**



Sulfuric acid

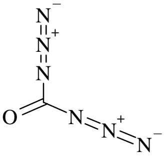
Thiele, J., *Ann.*, 1893, **273**, 148—149, 151

It decomposes non-explosively on heating, but ignites in contact with conc. sulfuric acid.

See other TETRAZOLES

0547. Carbonic diazide (Carbonyl azide)

[14435-92-8] **CN_6O**



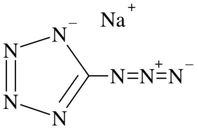
1. Chapman, L. E. *et al., Chem. & Ind.*, 1966, 1266
2. Kesting, W., *Ber.*, 1924, **57**, 1321
3. Curtius, T. *et al., Ber.*, 1894, **27**, 2684

It is a violently explosive solid, which should be used only in solution, and on a small scale [1]. It exploded violently under ice-water [2], or on exposure to bright light [3].

See other ACYL AZIDES, IRRADIATION DECOMPOSITION INCIDENTS

0548. Sodium 5-azidotetrazolide

[35038-45-0] **CN_7Na**



Marsh, F. D., *J. Org. Chem.*, 1972, **37**, 2967, 2969

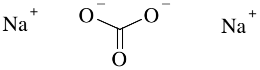
Readily formed from cyanogen bromide and sodium azide in aqueous solution at 0°C, it is extremely sensitive to friction, heat or pressure. A dry sample under vacuum at 1 mbar will detonate on rapid admission of air.

See 5-Azidotetrazole

See other FRICTIONAL INITIATION INCIDENTS, HIGH-NITROGEN COMPOUNDS, *N*-METAL DERIVATIVES, TETRAZOLES

0549. Sodium carbonate

[497-19-8] **CNa_2O_3**



HCS 1980, 832

Acidic reaction liquor

1. Anon., *Loss Prev. Bull.*, 1978, (023), 138
2. Anon., *Sichere Chemiearbeit*, 2000, **52**(2), 22

Use of sodium carbonate to neutralise the acid produced during methylation with dimethyl sulfate in a 2-phase system led to severe frothing, and the agitator was turned off to allow it to abate. When agitation was restarted, violent foaming from mixing of the separated acid and alkaline layers ejected 2 t of the reactor contents (remedy worse than ailment!) Use of magnesium oxide to neutralise acid without gas evolution was recommended [1]. Viscous acid waste was neutralised in drum by addition of solid carbonate. When visible bubbles ceased it was assumed reaction was complete and the drum was closed. The assumption was false, leading to a lost eye when pressure build-up blew the lid from the drum. Agitation could have prevented this [2].

See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS, NEUTRALISATION INCIDENTS

Ammonia, Silver nitrate

See Silver nitrate: Ammonia, etc.

An aromatic amine, A chloronitro compound

MCA Case History No. 1964

An unspecified process had been operated for 20 years using synthetic sodium carbonate powder (soda-ash) to neutralise the hydrogen chloride as it was formed by interaction of the amine and chloro compound in a non-aqueous (and probably flammable) solvent in a steel reactor. Substitution of the powdered sodium carbonate by the crystalline sodium carbonate—sodium hydrogencarbonate double salt (‘trona, natural soda’) caused a reduction in the rate of neutralisation, the reaction mixture became more acid, and attack on the steel vessel led to contamination by iron. These changed conditions initiated exothermic side reactions, which eventually ran out of control and caused failure of the reactor. Subsequent laboratory work confirmed this sequence and showed that presence of dissolved iron(III) was necessary to catalyse the side reactions.

See Sulfuric acid, below

See other CATALYTIC IMPURITY INCIDENTS, NEUTRALISATION INCIDENTS

2,4-Dinitrotoluene

See 2,4-Dinitrotoluene: Alkali

Fluorine

See Fluorine: Metal salts

Hydrogen peroxide
See CRYSTALLINE HYDROGEN PEROXIDATES

Lithium
See Lithium: Sodium carbonate

Phosphorus pentaoxide
See Tetraphosphorus decaaoxide: Inorganic bases

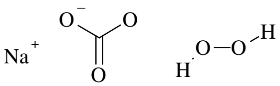
Sodium sulfide, Water
See SMELT: Water

Sulfuric acid
MCA Case History No. 888
Lack of any mixing arrangements caused stratification of strong sulfuric acid and (probably) sodium carbonate solutions in the same tank. When gas evolution caused intermixing of the layers, a violent eruption of the tank contents occurred.
See An aromatic amine, etc., above
See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS

2,4,6-Trinitrotoluene
See 2,4,6-Trinitrotoluene: Added impurities
See other INORGANIC BASES, METAL OXONON-METALLATES

0550. Sodium carbonate hydrogen peroxidate (‘Sodium percarbonate’)

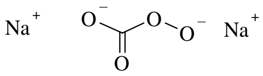
[15630-89-4] **$CNa_2O_3.1.5H_2O_2$**



See entry CRYSTALLINE HYDROGEN PEROXIDATES

0551. Sodium monoperoxycarbonate

[4452-58-8] **CNa_2O_4**



Acetic anhydride
See Sodium carbonate hydrogen peroxidate: Acetic anhydride
See other PEROXOACID SALTS

†0552. Carbon monoxide

[630-08-0] **CO**

$O\overset{+}{\equiv}C^{-}$

NSC 415, 1976; *FPA H57*, 1977 (cylinder); *HCS 1980*, 282

Aluminium, Aluminium halides
See Aluminium: Aluminium halides, Carbon oxides

Copper(I) perchlorate
See Copper(I) perchlorate, Alkenes, etc.

Dinitrogen oxide
See Dinitrogen oxide: Carbon monoxide

Fluorine, Oxygen
See Bis(fluoroformyl) peroxide

Hydrogen, Oxygen
See Oxygen: Carbon monoxide, Hydrogen

Interhalogens MRH values show % of interhalogen
See Bromine pentafluoride: Acids, etc. MRH 3.05/tr.
Bromine trifluoride: Carbon monoxide MRH 2.47/71
Iodine heptafluoride: Carbon, etc.

Metal oxides
See Caesium oxide: Halogens, etc.
Iron(III) oxide: Carbon monoxide
Silver(I) oxide: Carbon monoxide

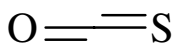
Metals
Sodium: Non-metal oxides
See Potassium: Non-metal oxides

Other reactants
Yoshida, 1980, 42
MRH values calculated for 11 combinations with oxidants are given.

Oxidants
See Chlorine dioxide: Carbon monoxide
Oxygen (Liquid): Liquefied gases
Peroxodisulfuryl difluoride: Carbon monoxide
See other NON-METAL OXIDES

†0553. Carbonyl sulfide (Carbon oxide sulfide)

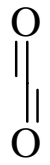
[463-58-1] **COS**



See related NON-METAL OXIDES, NON-METAL SULFIDES

0554. Carbon dioxide

[124-38-9] **CO_2**



NSC 682, 1980; *HCS 1980*, 279 (cylinder) 280 (solid)

Acrylaldehyde
See Acrylaldehyde: Acids

Aluminium, Aluminium halides
See Aluminium: Aluminium halides, Carbon oxides

Aziridine
See Aziridine: Acids

Barium peroxide
See Barium peroxide: Non-metal oxides

Caesium oxide
See Caesium oxide: Halogens, etc.

Flammable materials

1. *BCISC Quart. Safety Summ.*, 1973, **44**(174), 10
2. Leonard, J. T. *et al., Inst. Phys. Conf. Ser.*, 1975, **27** (Static Electrif.), 301—310
3. Anon., *Chem. Eng. News*, 1976, **54**(30), 18
4. Collocott, S. J. *et al., IEE Proc. part A*, 1980, **127**, 119—120
5. Moffat, M., *Fire Prot.*, 1980, (7), 9
6. Kletz, T. A., *Loss Prev. Bull.*, 1984, (056), 9

Dangers attached to the use of carbon dioxide in fire prevention and extinguishing systems in confined volumes of air and flammable vapours are discussed. The main hazard arises from the production of very high electrostatic charges, due to the presence of small frozen particles of carbon dioxide generated during expanding discharge of the compressed gas. Highly incendive sparks (5—15 mJ at 10—20 kV) readily may be produced. Nitrogen is preferred as an inerting gas for enclosed volumes of air and flammable gases or vapours [1]. The electrostatic hazard in discharge of carbon dioxide in tank fire-extinguishing systems is associated with the plastics distribution horns, and their removal eliminated the hazard [2]. Alternatively, a metal sleeve may be fitted inside the plastics horn [3]. The accumulation of charge during discharge of a portable extinguisher has also been studied and found potentially hazardous [4]. The latter hazard is minimised in a statement to clarify the overall situation, which emphasizes the need for avoiding the use of liquid carbon dioxide for inerting purposes [5]. Previous accidents involving carbon dioxide as the cause of explosions are reviewed [6].

Hydrazine, Stainless steel
See Hydrazine: Carbon dioxide, Stainless steel

Metal acetylides

See Monolithium acetylide—ammonia: Gases
Monopotassium acetylide: Non-metal oxides
Rubidium acetylide: Non-metal oxides
Sodium acetylide: Non-metal oxides

Metal hydrides

See Aluminium hydride: Carbon dioxide
Lithium tetrahydroaluminate: Bis(2-methoxyethyl) ether

Metals

1. Hartmann, I., *Ind. Eng. Chem.*, 1948, **40**, 756
2. Rhein, R. A., *Rept. No. CR-60125*, Washington, NASA, 1964

Dusts of magnesium, zirconium, titanium and some magnesium—aluminium alloys [1], and (when heated) of aluminium, chromium and manganese [2], when suspended in carbon dioxide atmospheres are ignitable and explosive, and several bulk metals will burn in the gas.

See Metals, Nitrogen below
Aluminium: Aluminium halides, Carbon oxides
Lithium: Non-metal oxides
Magnesium: Carbon dioxide, etc.
Potassium: Non-metal oxides
Potassium—sodium alloy: Carbon dioxide
Sodium: Non-metal oxides
Titanium: Carbon dioxide
Uranium: Carbon dioxide

Metals, Nitrogen

Rhein, R. A., *Rept. No. CR-60125*, Washington, NASA, 1964

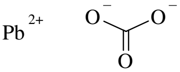
Powdered beryllium, cerium, cerium alloys, thorium, titanium, uranium and zirconium ignite on heating in mixtures of carbon dioxide and nitrogen; ignition temperatures were determined. Aluminium, chromium, magnesium and manganese ignite only in the absence of nitrogen.

Metals, Sodium peroxide

See Sodium peroxide: Metals, Carbon dioxide
See other NON-METAL OXIDES

0555. Lead carbonate

[598-63-0] **CO_3Pb**

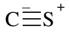


HCS 198, 586

Fluorine
See Fluorine: Metal salts

0556. Carbon sulfide

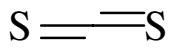
[2944-05-0] **CS**



Pearson, T. G., *School Sci. Rev.*, 1938, **20**(78), 189
The gaseous radical polymerises explosively.
See other NON-METAL SULFIDES

†0557. Carbon disulfide

[75-15-0] **CS_2**



(*MCA SD-12*, 1967); *NSC 341*, 1977; *FPA H34*, 1975; *HCS 1980*, 281; *RSC Lab. Hazard Data Sheet No. 7*, 1982

1. Thiem, F., *Chem. Technik*, 1979, **31**, 313—314
2. Briggs, A. G. *et al., Chem. Brit.*, 1982, **18**, 27
3. Bothe, H. *et al., Loss Prevention and Safety Promotion in the Process Industries* Vol. II (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 327, Amsterdam, Elsevier, 1995

Carbon disulfide vapour, alone or mixed with nitrogen, did not decompose explosively in the range 0.4—2.1 bar/88—142°C when initiated with high energy sparks or a hot wire at 700—900°C. The endothermic sulfide (ΔH_f° (l) +115.3 kJ/mol, 1.52 kJ/g) will, however, decompose explosively to its elements with mercury fulminate initiation [1]. A screening jacket filled with carbon disulfide was used to surround the reaction tube used in flash photolysis experiments. When the quartz lamp was discharged, some vapour of the disulfide which had leaked out ignited in the radiation flash and exploded. Care is also necessary with the vapour and other UV sources [2]. Ignition of vapour air mixes by laser has been studied [3].
See other IRRADIATION DECOMPOSITION INCIDENTS

Air, Rust

1. Mee, A. J., *School Sci. Rev.*, 1940, **22**(86), 95
2. Dickens, G. A., *School Sci. Rev.*, 1950, **31**(114), 264
3. Anon., *J. Roy. Inst. Chem.*, 1956, **80**, 664
4. Thompson, E., private comm., 1981

Disposal of 2 l of the solvent into a rusted iron sewer caused an explosion. Initiation of the solvent—air mixture by rust was suspected [1]. A hot gauze falling from a tripod into a laboratory sink containing some carbon disulfide initiated two explosions [2]. It is a very hazardous solvent because of its extreme volatility and flammability. The vapour or liquid has been known to ignite on contact with steam pipes, particularly if rusted [3]. When a winchester of the solvent fell off a high shelf and broke behind a rusted steel cupboard, ignition occurred [4].

Alkali metals

1. Steimecke, G. *et al., Phos. Sulfur*, 1979, **7**, 49
2. Moradpour, A. *et al., J. Chem. Educ.*, 1986, **62**, 1016
3. Staudinger, H., *Z. Angew. Chem.*, 1922, **35**, 659

Attempts to follow a published procedure for the preparation of 1,3-dithiole-2-thione-4,5-dithiolate salts [1], involving reductive coupling of carbon disulfide with alkali metals, have led to violent explosions with potassium metal, but not with sodium [2]. However, mixtures of carbon disulfide with potassium—sodium alloy, potassium, sodium, or lithium are capable of detonation by shock, though not by heating. The explosive power decreases in the order given above, and the first mixture is more shock-sensitive than mercury fulminate [3].

See Metals, below

Amines

1. Anon., Personal communication, 1991
2. Editor's comments.

Carbon disulphide was used as an extraction solvent when analysing epoxy resins. On one occasion, adding to a hardener produced a vigorous fume-off leaving a residue looking like sulfur [1]. Amines and complexes thereof are used as hardeners, and the reaction with, especially, polyamines to give dithiocarbamates is surprisingly exothermic [2].

Chlorine, Sodium *aci*-nitromethanide

See Sodium *aci*-nitromethanide: Carbon disulfide, etc.

Halogens

See Chlorine: Carbon disulfide
Fluorine: Sulfides

Metal azides

Mellor, 1947, Vol. 8, 338

Carbon disulfide and aqueous solutions of metal azides interact to produce metal azidodithioformates, most of which are explosive with varying degrees of power and sensitivity to shock or heat.

See Azidodithioformic acid

See also Sodium azide: Carbon disulfide

Metals MRH Zinc 2.43/63

See Alkali metals, above
Aluminium: Carbon disulfide
Sodium: Sulfides, etc.
Zinc: Carbon disulfide

Other reactants

Yoshida, 1980, 281

MRH values calculated for 16 combinations, largely with oxidants, are given.

Oxidants

See Halogens, above

Dinitrogen tetraoxide: Carbon disulfide

Nitrogen oxide: Carbon disulfide

Permanganic acid: Organic materials

Phenylcopper—triphenylphosphine complexes

Camus, A. *et al., J. Organomet. Chem.*, 1980, **188**, 390

The bis- or tris-complexes of phenylcopper with triphenylphosphine react violently and exothermically with carbon disulfide, even at 0°C. Suitable control procedures are described.

See other ENDOTHERMIC COMPOUNDS, NON-METAL SULFIDES

0558. Titanium carbide

[12070-08-5] **CTi**

$Ti^{4+} \quad C^{4-}$

MCA Case History No. 618

A violent, and apparently spontaneous, dust explosion occurred while the finely ground carbide was being removed from a ball-mill. Static initiation seems a likely possibility.

See entry DUST EXPLOSION INCIDENTS, REFRACTORY POWDERS

See other METAL NON-METALLIDES

0559. Uranium carbide

[12070-09-6] **CU**

$U^{4+} \quad C^{4-}$

Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163

The finely divided carbide is pyrophoric.

See other METAL NON-METALLIDES, PYROPHORIC MATERIALS

0560. Tungsten carbide

[12070-12-1] **CW**

$W^{4+} \quad C^{4-}$

Fluorine

See Fluorine: Metal acetylides and carbides

Nitrogen oxides

Mellor, 1946, Vol. 5, 890

At about 600°C, the carbide ignites and incandesces in dinitrogen mono- or tetra-oxides.

See other METAL NON-METALLIDES

0561. Ditungsten carbide

[12070-13-2] **CW_2**

W^{2+} C^{4-} W^{2+}

Oxidants

Mellor, 1946, Vol. 5, 890

The carbide burns incandescently at red heat in contact with dinitrogen mono- or tetra- oxides.

See Fluorine: Metal acetylides and carbides

See other METAL NON-METALLIDES

0562. Zirconium carbide

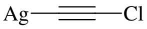
[12070-14-3] **CZr**

Zr^{4+} C^{4-}

See entry REFRACTORY POWDERS

0563. Silver chloroacetylide

[ ] **C_2AgCl**



Kirk-Othmer, 1964, Vol. 5, 204

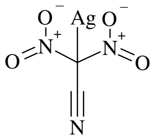
Explosive, even when wet or under water.

See other SILVER COMPOUNDS

See related HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

0564. Silver cyanodinitromethanide

[12281-65-1] **$C_2AgN_3O_4$**



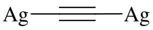
Parker, C. O. *et al., Tetrahedron*, 1962, **17**, 86

A sample in a m.p. capillary exploded at 196°C, shattering the apparatus.

See other POLYNITROALKYL COMPOUNDS, SILVER COMPOUNDS

0565. Silver acetylide

[7659-31-6] **C_2Ag_2**



1. Miller, 1965, Vol. 1, 486

2. Bailar, 1973, Vol. 3, 102
3. Reynolds, R. J. *et al., Analyst*, 1971, **96**, 319
4. Koehn, J., *Chem Abs.*, 1979, **91**, 7164

Silver acetylide is a more powerful detonator than the copper derivative, but both will initiate explosive acetylene-containing gas mixtures [1]. It decomposes violently when heated to 120—140°C [2]. Formation of a deposit of this explosive material was observed when silver-containing solutions were aspirated into an acetylene-fuelled atomic absorption spectrometer. Precautions to prevent formation are discussed [3]. The effect of ageing for 16 months on the explosive properties of silver and copper acetylides has been studied. Both retain their hazardous properties for many months, and the former is the more effective in initiating acetylene explosions [4].

See other METAL ACETYLIDES, SILVER COMPOUNDS

0566. Silver acetylide—silver nitrate

[15336-58-0] **$C_2Ag_2.AgNO_3$**

1. Baker, W. E. *et al., Chem. Eng. News*, 1965, **43**(49), 46
2. Hogan, V. D. *et al., OTS Rept. AD 419 625*, Washington, US Dept. Comm., 1960
3. Benham, R. A., *Chem. Abs.*, 1981, **94**, 142109

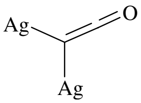
The dry complex is exploded by high-intensity light pulses, or by heat or sparks. As a slurry in acetone, it is stable for a week if kept dark [1]. The complex explodes violently at 245°C/1 bar and at 195°C/1.3 mbar [2], or on exposure to light [3].

See other IRRADIATION DECOMPOSITION INCIDENTS, SILVER COMPOUNDS

See related METAL ACETYLIDES

0567. Disilver ketenide (Oxovinylidenedisilver)

[27378-01-4] **C_2Ag_2O**



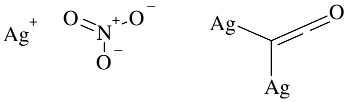
1. Blues, E. T. *et al., Chem. Comm.*, 1970, 699
2. Bryce-Smith, D. *et al., J. Chem. Soc., Perk. Trans. 2*, 1993, (9), 1631.

This and its pyridine complex explode violently if heated or struck [1] (but see below). More data on the stability of disilver ketenide and its complexes is contained in [2].

See other SILVER COMPOUNDS

0568. Disilver ketenide—silver nitrate

[ ] **$C_2Ag_2O.AgNO_3$**



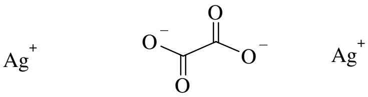
1. Bryce-Smith, D., *Chem. & Ind.*, 1975, 154
2. Blues, E. T. *et al., Chem. Comm.*, 1970, 701

The red complex is more dangerously explosive than the ketenide itself, now described as mildly explosive in the dry state when heated strongly or struck [1]. It was previously formulated as a 2:1 complex [2].

See other SILVER COMPOUNDS

0569. Silver oxalate

[533-51-7] **$C_2Ag_2O_4$**



1. Sidgwick, 1950, 126
2. Anon., *BCISC Quart. Safety Summ.*, 1973, **44**, 19
3. Kabanov, A. A. *et al., Russ. Chem. Rev.*, 1975, **44**, 538
4. MacDonald, J. Y. *et al., J. Chem. Soc.*, 1925, **127**, 2625
5. Waltenberger-Razniewska, M. *et al., Chem. Abs.*, 1982, **96**, 203117
6. Ullmann, 1993, Vol A24, 161

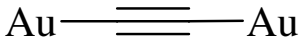
Above 140°C its exothermic decomposition to metal and carbon dioxide readily becomes explosive [1]. A 1 kg batch which had been thoroughly dried at 50°C exploded violently when mechanical grinding in an end-runner mill was attempted [2]. Explosions have been experienced when drying the oxalate as low as 80°C [6]. It is a compound of zero oxygen balance. The explosion temperature of the pure oxalate is lowered appreciably (from 143 to 122°C) by application of an electric field [3]. The salt prepared from silver nitrate with excess of sodium oxalate is much less stable than that from excess nitrate [4]. Decomposition at 125°C in glycerol prevents explosion in the preparation of silver powder [5].

See ELECTRIC FIELDS

See other METAL OXALATES, SILVER COMPOUNDS

0570. Gold(I) acetylide

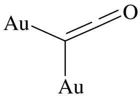
[70950-00-4] **C_2Au_2**



1. Mellor, 1946, Vol. 5, 855
2. Matthews, J. A. *et al., J. Amer. Chem. Soc.*, 1900, **22**, 110

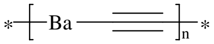
Produced by action of acetylene on sodium gold thiosulfate (or other gold salts), the acetylide is explosive and readily initiated by light impact, friction or rapid heating to 83°C [1]. This unstable detonator is noted for high brisance [2].
See other GOLD COMPOUNDS, METAL ACETYLIDES

0571. Digold(I) ketenide
[54086-41-8] **C_2Au_2O**



Blues, E. T. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 513—514
The ketenide is shock-sensitive when dry, and it or its complexes with tertiary heterocyclic bases (pyridine, methylpyridines, 2,6-dimethylpyridine or quinoline) explode when heated above 100°C.
See other GOLD COMPOUNDS

0572. Barium acetylide
[12070-27-8] **$(C_2Ba)_n$**

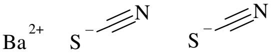


Air, or Hydrogen, or Hydroxylic compounds
Masdupay, E. *et al., Compt. rend.*, 1951, **232**, 1837—1839
It is much more reactive than the diacetylide, and ignites in contact with water or ethanol in air. It may incandesce on heating to 150°C under vacuum or hydrogen, the product from the latter treatment being very pyrophoric owing to the presence of pyrophoric carbon.

Halogens
Mellor, 1946, Vol. 5, 862
Barium acetylide incandesces with chlorine, bromine or iodine at 140, 130 or 122°C respectively.

Selenium
Mellor, 1946, Vol. 5, 862
A mixture incandesces when heated to 150°C.
See other METAL ACETYLIDES

0573. Barium thiocyanate
[2092-17-3] **$C_2BaN_2S_2$**



Potassium chlorate
See Potassium chlorate: Metal thiocyanates

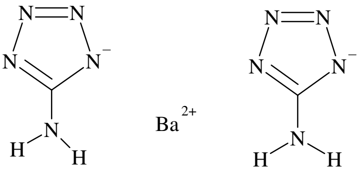
Sodium nitrite

See Sodium nitrite: Potassium thiocyanate

See related METAL CYANIDES

0574. Barium 5,5′-azotetrazolide

[87478-73-7] **C_2BaN_{10}**

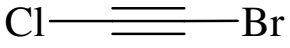


See entry METAL AZOTETRAZOLIDES

See other TETRAZOLES

0575. Bromochloroacetylene

[25604-70-0] **C_2BrCl**



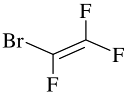
Houben-Weyl, 1977, Vol. 5.2a, 604 (footnote 6)

Highly explosive and unstable.

See other HALOACETYLENE DERIVATIVES

†0576. Bromotrifluoroethylene

[598-73-2] **C_2BrF_3**



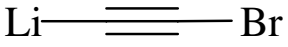
Oxygen

See Oxygen (Gas): Halocarbons

See other HALOALKENES

0577. Lithium bromoacetylide

[ ] **C_2BrLi**

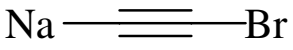


See Sodium bromoacetylide (next below); Lithium chloroacetylide; Lithium trifluoropropynide; Sodium chloroacetylide

See other HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

0578. Sodium bromoacetylide

[ ] **C_2BrNa**



Cradock, S. *et al., J. Chem. Soc., Dalton Trans.*, 1978, 760

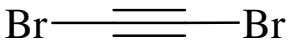
The dry material (perhaps the ultimate 'carbene precursor') is an extremely shock-sensitive explosive.

See Lithium bromoacetylide; Lithium chloroacetylide; Lithium trifluoropropynide; Sodium chloroacetylide

See other HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

0579. Dibromoacetylene

[624-61-3] **C_2Br_2**



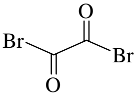
Rodd, 1951, Vol. 1A, 284

It ignites in air and explodes on heating.

See other HALOACETYLENE DERIVATIVES

0580. Oxalyl dibromide

[15219-34-8] **$C_2Br_2O_2$**



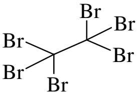
Potassium

See Potassium: Oxalyl dihalides

See other ACYL HALIDES

0581. Hexabromoethane

[594-73-0] **C_2Br_6**



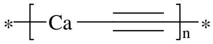
Hexacyclohexyldilead

See Hexacyclohexyldilead: Halocarbons

See other HALOALKANES

0582. Calcium acetylide (Calcium carbide)

[75-20-7] **$(C_2Ca)_n$**



HCS 1980, 264

1. Anon., *Ind. Safety Bull.*, 1940, **8**, 41
2. Déribère, M., *Chem. Abs.*, 1936, **30**, 8169.8
3. Orlov, V. N., *Chem. Abs.*, 1975, **83**, 168138
4. Babaitsev, I. V. *et al, Metallurg. (Moscow)*, 2000, (3), 32

Use of a steel chisel to open a drum of carbide caused an incendive spark which ignited traces of acetylene in the drum. The non-ferrous tools normally used for this purpose should be kept free from embedded ferrous particles [1]. If calcium carbide is warm when filled into drums, absorption of the nitrogen from the trapped air may enrich the oxygen content up to 28%. In this case, less than 3% of acetylene (liberated by moisture) is enough to form an explosive mixture, which may be initiated on opening the sealed drum. Other precautions are detailed [2]. Use of carbon dioxide to purge carbide drums, and of brass or bronze non-sparking tools to open them are advocated [3]. The dust explosion characteristics of calcium carbide powder in air have been studied [4].

Calcium hypochlorite
See Calcium hypochlorite

Halogens
Mellor, 1946, Vol. 5, 862
The acetylide incandesces with chlorine, bromine or iodine at 245, 350 or 305°C, respectively. Strontium and barium acetylides are more reactive.

Hydrogen chloride MRH 3.97/54
Mellor, 1946, Vol. 5, 862
Incandescence on warming; strontium and barium acetylides are similar.

Iron(III) chloride, Iron(III) oxide
Partington, 1967, 372
The carbide is an energetic reducant. A powdered mixture with iron oxide and chloride burns violently when ignited, producing molten iron.
See other THERMITE REACTIONS

Lead difluoride
Mellor, 1946, Vol. 5, 864
Incandescence on contact at ambient temperature.

Magnesium
Mellor, 1940, Vol. 4, 271
A mixture incandesces when heated in air.

Methanol

Unpublished observations, 1951

Interaction of calcium carbide with methanol to give calcium methoxide is very vigorous, but subject to an induction period of variable length. Once reaction starts, evolution of acetylene gas is very fast, and a wide-bore condenser and adequate ventilation are necessary.

See other GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS

Other reactants

Yoshida, 1980, 223

MRH values calculated for 8 combinations with various reagents are given.

Perchloryl fluoride

See Perchloryl fluoride: Calcium acetylide

Selenium

See Selenium: Metal acetylides

Silver nitrate

Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 334

Addition of calcium acetylide to silver nitrate solution precipitates silver acetylide, a highly sensitive explosive. Copper salt solutions would behave similarly.

See other METAL ACETYLIDES

Sodium peroxide MRH 3.01/86

See Sodium peroxide: Calcium acetylide

Sulfur MRH 4.35/33

See Sulfur: Metal acetylides

Tin(II) chloride

Mellor, 1941, Vol. 7, 430

A mixture can be ignited with a match, and reduction to metallic tin proceeds with incandescence.

Water

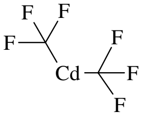
1. Jones, G. W. *et al., Explosions in Med. Press. Generators, Invest. Rept. 3775*, Washington, US Bur. Mines, 1944
2. Moll, H., *Chem. Weekbl.*, 1933, **30**, 108

At the end of a generation run, maximum temperature and high moisture content of acetylene may cause the finely-divided acetylide to overheat and initiate explosion of pressurised gas [1]. During analysis of technical carbide by addition of water, the explosive mixture formed in the unpurged reaction vessel exploded, ignited either by excessive local temperature or, possibly, by formation of crude phosphine from the phosphide present as impurity in the carbide [2].

See other METAL ACETYLIDES, REDUCANTS

0583. Bis(trifluoromethyl)cadmium

[33327-66-1] **C_2CdF_6**



1. Eujen, R.*et al., J. Organomet. Chem.,* 1995, **503**(2), C51
2. Eujen, R. *et al., Z. Naturforsch., B:*, 1998, **53**(12), 1455

The uncomplexed compound decomposes to difluorocarbene at —5° and explodes violently on warming to room temperature [1] or on exposure to air [2].

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

0584. Bis(trifluoromethyl)cadmium—1,2-dimethoxyethane adduct

[33327-66-1] **$C_2CdF_6.C_4H_{10}O_2$**

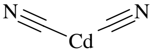
Ontiveros, C. D. *et al., Inorg. Synth.*, 1986, **24**, 57

It may ignite in air if not thoroughly dry and pure.

See related ALKYLMETALS

0585. Cadmium cyanide

[542-83-6] **C_2CdN_2**



It is moderately endothermic (ΔH_f° (s) +163.2 kJ/mol, 0.99kJ/g)

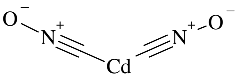
Magnesium

See Magnesium: Metal cyanides

See other ENDOTHERMIC COMPOUNDS, METAL CYANIDES

0586. Cadmium fulminate

[42994-95-6] **$C_2CdN_2O_2$**



It is a moderately endothermic compound (ΔH_f° (s) +163.2 kJ/mol, 0.80 kJ/g).

See entry ENDOTHERMIC COMPOUNDS, METAL FULMINATES

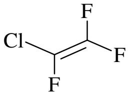
0587. Cerium carbide

[12012-32-7] **C_2Ce**

See Lanthanum carbide

†0588. Chlorotrifluoroethylene

[79-38-9] **C_2ClF_3**



Bromine, Oxygen
See Bromine: Chlorotrifluoroethylene, Oxygen

Chlorine perchlorate
See Chlorine perchlorate: Chlorotrifluoroethylene

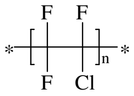
1,1-Dichloroethylene
See 1,1-Dichloroethylene: Chlorotrifluoroethylene

Ethylene
See Ethylene: Chlorotrifluoroethylene

Oxygen
See Oxygen (Gas): Halocarbons (references 3,4)
See other HALOALKENES

0589. Poly(chlorotrifluoroethylene)

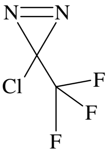
[9002-83-9] **$(C_2ClF_3)_n$**



Aluminium
See Aluminium: Halocarbons
See related HALOALKANES

0590. 3-Chloro-3-trifluoromethyldiazirine

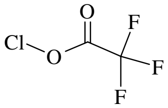
[58911-30-1] **$C_2ClF_3N_2$**



Moss. R. A. *et al., J. Amer. Chem. Soc.*, 1981, **103**, 6168—6169
The potentially explosive compound was used safely as a solution in pentane.
See other DIAZIRINES

0591. Trifluoroacetyl hypochlorite

[65597-25-3] **$C_2ClF_3O_2$**

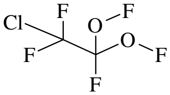


1. Tari, I. *et al., Inorg. Chem.*, 1979, **18**, 3205—3208
2. Schack, C. J. *et al.*, US Pat. Appl. 47,588, 1979
3. Gard, G. L. *et al., Inorg. Chem.*, 1965, **4**, 594
4. Rozen, S. *et al., J. Org. Chem.*, 1980, **45**, 677

Thermally unstable at 22°C and explosive in the gas phase at pressures above 27—62 mbar [1], there is also an explosion hazard during distillation and trapping at —78°C [2]. The crude (80%) material prepared by action of 3% fluorine in nitrogen on sodium trifluoroacetate [3] has, however, been used synthetically for 3 years without mishap [4].
See other ACYL HYPOHALITES

0592. 2-Chloro-1,1-bis(fluorooxy)trifluoroethane

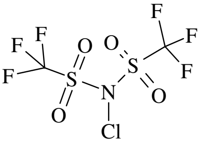
[72985-56-9] **$C_2ClF_5O_2$**



Sekiya, A. *et al., Inorg. Chem.*, 1980, **19**, 1330
Extremely explosive, detonation of a 1 mmol sample in a vacuum line led to ‘impressive damage’.
See other BIS(FLUOROOXY)PERHALOALKANES

0593. *N*-Chlorobis(trifluoromethanesulfonyl)imide

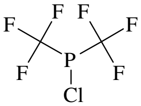
[91742-17-5] **$C_2ClF_6NO_4S_2$**



Foropoulos, J. *et al., Inorg. Chem.*, 1984, **23**, 3721
During preparation of the title compound from the imide and chlorine fluoride, initially at —111°C with slow warming during 12 h to 0°C, the scale should be

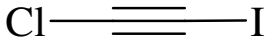
limited to 40 mmol or below. Forceful explosions occurred on several occasions when this scale was exceeded, but care is necessary on any scale of working.
See other N-HALOGEN COMPOUNDS

0594. Bis(trifluoromethyl)chlorophosphine
[650-52-2] **C_2ClF_6P**



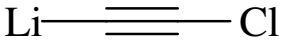
491M, 1975, 60
It ignites in air.
See other ALKYLHALOPHOSPHINES

0595. Chloroiodoacetylene (Chloroiodoethyne)
[25604-71-1] **C_2ClI**



Houben-Weyl, 1977, Vol. 5.2a, 604 (footnote 6)
Highly unstable and explosive.
See other HALOACETYLENE DERIVATIVES

0596. Lithium chloroacetylide (Lithium chloroethynide)
[6180-21-8] **C_2ClLi**



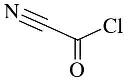
1. Cadiot, P., *BCISC Quart. Safety Summ.*, 1965, **36**(142), 27
2. Sinden, B. B. *et al., J. Org. Chem.*, 1980, **45**, 2773

During its synthetic use in liquid ammonia, some of the salt separated as a crust owing to evaporation of solvent, and exploded violently. Such salts are stable in solution, but dangerous in the solid state. Evaporation of ammonia must be prevented or made good until unreacted salt has been decomposed by addition of ammonium chloride [1]. An improved preparation of the lithium derivative is available [2].
See Lithium bromoacetylide; Lithium trifluoropropynide; Sodium bromoacetylide; Sodium chloroacetylide

Methyl chloroformate
Acheson, R. M. *et al., J. Chem. Res.; Synop.*, 1986, (10), 378—379
An attempt to prepare methyl chloropropiolate from chloroethynyllithium and methyl chloroformate led to an explosion.
See other HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

0597. Cyanoformyl chloride

[4474-17-3] **C_2ClNO**

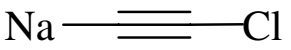


Water

Appel, R. *et al., Angew. Chem. (Intern. Ed.)*, 1983, **22**, 785
Reaction with water is violent, forming triazinetricarboxylic acid.
See other ACYL HALIDES, CYANO COMPOUNDS

0598. Sodium chloroacetylide (Sodium chloroethynide)

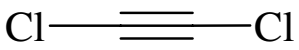
[ ] **C_2ClNa**



Viehe, H. G., *Chem. Ber.*, 1959, **92**, 1271
Though stable and usable in solution, the sodium salt, like the lithium and calcium salts, is dangerously explosive in the solid state.
See Lithium bromoacetylide; Lithium chloroacetylide; Sodium bromoacetylide; Lithium trifluoropropynide
See other HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

0599. Dichloroacetylene (Dichloroethyne)

[7572-29-4] **C_2Cl_2**



1. Wotiz, J. H. *et al., J. Org. Chem.*, 1961, **26**, 1626
2. Ott, E., *Ber.*, 1942, **75**, 1517
3. Kirk-Othmer, 1964, Vol. 5, 203—205
4. Siegel, J. *et al., J. Org. Chem.*, 1970, **35**, 3199
5. Riemschneider, R. *et al., Ann.*, 1961, **640**, 14
6. *MCA Case History No. 1989*
7. Kende, A. S. *et al., Synthesis*, 1982, 455
8. Kende. A. S. *et al., Tetrahedron Lett.*, 1982, **23**, 2369, 2373
9. Denis, J. N. *et al., J. Org. Chem.*, 1987, **52**, 3461—3462

Dichloroacetylene is rather endothermic (ΔH_f° (g) +149.4 kJ/mol, 1.57 kJ/g) and a heat-sensitive explosive gas which ignites in contact with air. However, its azeotrope with diethyl ether (55.4% dichloroacetylene) is not explosive and is stable to air [1][2]. It is formed on catalysed contact between acetylene and chlorine, or sodium hypochlorite at low temperature; or by the action of alkali upon polychloro-ethane and -ethylene derivatives, notably trichloroethylene [3]. A safe synthesis has been described [4]. Ignition of a 58 mol% solution in ether on exposure to air of high humidity, and violent explosion of a conc. solution in carbon tetrachloride shortly after exposure to air have been reported. Stirring the ethereal solution with tap water usually caused ignition and explosion [5]. Dichloroacetylene had been collected without incident on 6 previous occasions as a dilute solution. When the cooling system was modified by lowering the temperature in the water separator, liquid chloroacetylene separated there and exploded when a stopcock was turned [6]. A safer low temperature preparation of material free of trichloroethylene has been described [7][8]. A practical high-yielding synthesis of dichloroacetylene involves addition of a catalytic amount of methanol to a mixture of trichloroethylene and potassium hydride in THF [9].

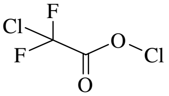
Trichloroethylene: Alkali, or: Epoxides

See Chlorocyanoacetylene

See Tetrachloroethylene: Sodium hydroxide

See other HALOACETYLENE DERIVATIVES

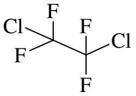
0600. Chlorodifluoroacetyl hypochlorite
[68674-44-2] **$C_2Cl_2F_2O_2$**



Unstable above 22°C and explosive in gas phase at pressures above 27—63 mbar.

See entry ACYL HYPOHALITES (reference 1)

0601. 1,2-Dichlorotetrafluoroethane
[76-14-2] **$C_2Cl_2F_4$**

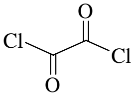


Aluminium

See Aluminium: Halocarbons

See other HALOALKANES

0602. Oxalyl dichloride (Oxalyl chloride)
[79-37-8] **$C_2Cl_2O_2$**



Alumina

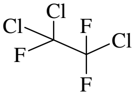
Kropp. P. J. *et al., J. Amer. Chem. Soc.*, 1993, **115**(8), 3071

Vigorous gas evolution (probably CO — Ed.) was produced when oxalyl chloride was adsorbed on alumina.

Dimethyl sulfoxide
See Dimethyl sulfoxide: Acyl halides

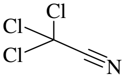
Potassium
See Potassium: Oxalyl dihalides
See other ACYL HALIDES

0603. 1,1,2,-Trichlorotrifluoroethane
[76-13-1] **$C_2Cl_3F_3$**



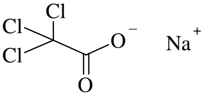
Metals
See Aluminium: Halocarbons
Barium: Halocarbons
Lithium: Halocabons
Samarium: 1,1,2-Trichlorotrifluoroethane
Titanium: Halocarbons
See other HALOALKANES

0604. Trichloroacetonitrile
[545-06-2] **C_2Cl_3N**



Ammonium chloride, Sodium azide
See 5-Trichloromethyltetrazole
See other CYANO COMPOUNDS

0605. Sodium trichloroacetate
[650-51-1] **$C_2Cl_3NaO_2$**

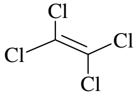


HCS 1980, 864

Doyle, W. H., *Loss Prev.*, 1969, **3**, 15
Energy of decomposition (in range 150—250°C) was measured as 0.23 kJ/g by DSC, and T_{ait24} was determined as 119°C by adiabatic Dewar tests, with an apparent energy of activation of 140 kJ/mol.
Bags of the salt ignited in storage (cause unknown) [1].
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

0606. Tetrachloroethylene

[127-18-4] **C_2Cl_4**



(*MCA SD-24*, 1971); *HCS 1980*, 887; *RSC Lab. Hazard Data Sheet No. 6*, 1982

Aluminium
See Aluminium: Halocarbons

Aluminium, Zinc oxide
Katz, S. *et al., Chem. Abs.*, 1981, **94**, 33106
The mixture is burned militarily to produce dense smoke.

Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Halocarbons

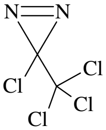
Metals
See Barium: Halocarbons
Lithium: Halocarbons

Sodium hydroxide
Mitchell, P. R., private comm., 1973
The presence of 0.5% of trichloroethylene as impurity in tetrachloroethylene during unheated drying over solid sodium hydroxide caused generation of dichloroacetylene. After subsequent fractional distillation, the volatile fore-run exploded.
See Dichloroacetylene
See also Trichloroethylene: Alkali
See other HALOALKENES

Zinc
J. A. Young, private communication, 1997
Distillation of tetrachloroethylene (formerly a dry-cleaning solvent) in new galvanised steel equipment produces traces of dichloroacetylene. This is toxic and may cause ill-health in those exposed. Should the acetylene chance to be concentrated (as in the sub-entry above), it is also very explosive. The galvanised metal becomes passivated in a few days and the effect was not found with other steels.
See Dichloroacetylene

0607a. 3-Chloro-3-trichloromethyldiazirine

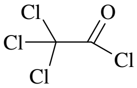
[35295-56-8] **$C_2Cl_4N_2$**



Liu, M. T. H., *Chem. Eng. News*, 1974, **52**(36), 3

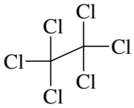
An ampoule of the compound exploded when scored with a file, indicating high shock-sensitivity.
See other DIAZIRINES

0607b. Trichloroacetyl chloride
[76-02-8] **C_2Cl_4O**



Acrylonitrile
See Acrylonitrile: Trichloroacetyl chloride
See other ACYL HALIDES

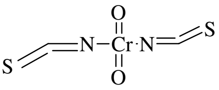
0608. Hexachloroethane
[67-72-1] **C_2Cl_6**



HCS 1980, 530

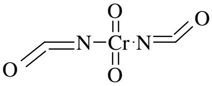
Metals
See Aluminium: Halocarbons
Zinc: Halocarbons
See other HALOALKANES

0609. Chromyl isothiocyanate
[ ] **$C_2CrN_2O_2S_2$**



Forbes, G. S. *et al., J. Amer. Chem. Soc.*, 1943, **65**, 2273
The salt, prepared in carbon tetrachloride solution, exploded feebly several times as the reaction proceeded. Oxidation of thiocyanate by chromium(VI) is postulated.
See related METAL CYANIDES

0610. Chromyl isocyanate
[ ] **$C_2CrN_2O_4$**



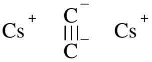
Forbes G. S. *et al., J. Amer. Chem. Soc.*, 1943, **65**, 2273

The product is stable during unheated vacuum evaporation of its solutions in carbon tetrachloride. Evaporation with heat at ambient pressure led to a weak explosion of the salt.

See related METAL CYANIDES

0611. Caesium acetylide

[22750-56-7] **C_2Cs_2**



Halogens

Mellor, 1946, Vol. 5, 848

It burns in all four halogens at or near ambient temperature.

Iron(III) oxide

Mellor, 1946, Vol. 5, 849

Incandescence on warming.

Lead dioxide

See Lead(IV) oxide: Metal acetylides

Mineral acids

Mellor, 1946, Vol. 5, 848

It ignites in contact with gaseous hydrogen chloride or its conc. aqueous solution, and explodes with nitric acid.

Non-metals

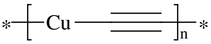
Mellor, 1946, Vol. 5, 848

Mixtures with boron or silicon react vigorously on heating.

See other METAL ACETYLIDES

0612. Copper(II) acetylide

[12540-13-5] **$(C_2Cu)_n$**



1. Urbanski, 1967, Vol. 3, 228
2. Bond, J., *Hazards from Pressure, IChE Symp. Ser. No. 102*, 37—44, Oxford, Pergamon, 1987
3. Anon., *Jahresber.*, 1987, 64; 1988, 140 (same incident)

Copper(II) acetylide (black or brown) is much more sensitive to impact, friction or heat than copper(I) acetylide (red-brown) which is used in electric fuses or detonators [1]. An explosion during maintenance work on a copper condenser in a methanol plant was attributed to copper acetylide deposits in the heat exchanger [2]. During internal inspection of an air-purged 15 year old 330 m^3 liquefied gas cylinder, it was noticed that there was a 2—3 cm layer of rust-like deposit at the bottom. As the inspection

proceded and the layer was disturbed, small flames were seen, and then a detonation occurred. The deposit was found to contain 20% of copper but less than 1% of sulfur, so was thought to be a mixture of rust and copper acetylide, friction-sensitive when dry [3].
See Silver acetylide (reference 4)
See also Dicopper(I) 1,3,5,7,9,11,13,15,17,19,21,23,25,27,29,31,33,35,37,39, -tetracontaeicosayne-1,40-diide
See also Dicopper(I) butadiynide
See other METAL ACETYLIDES

0613. Copper(II) cyanide
[544-92-3] **C_2CuN_2**

$$N{\equiv}C^{-}\quad Cu^{2+}\quad {}^{-}C{\equiv}N$$

Magnesium
See Magnesium: Metal cyanides
See other METAL CYANIDES (AND CYANO COMPLEXES)

0614. Copper(II) fulminate
[22620-90-2] **$C_2CuN_2O_2$**

$$O^{-}{-}N^{+}{\equiv}C^{-}\quad Cu^{2+}\quad {}^{-}C{\equiv}N^{+}{-}O^{-}$$

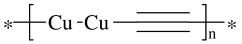
See entry METAL FULMINATES

0615. Copper(II) thiocyanate
[15192-76-4] **$C_2CuN_2S_2$**

$$N{\equiv}{-}S{-}Cu{-}S{-}{\equiv}N$$

Tudela, D., *J. Chem. Educ.*, 1993, **70**(2), 174
On addition to boiling water, black cupric thiocyanate converts to the white cuprous salt with violent gas evolution. It is suggested that the gas is hydrogen cyanide, though carbon dioxide seems probable.
See related METAL CYANATES

0616. Dicopper(I) acetylide
[1117-94-8] **$(C_2Cu_2)_n$**



1. Mellor, 1946, Vol. 5, 851, 852
2. Rutledge, 1968, 84—85

3. Morita, S., *J. Soc. High Press. Gas Ind.*, 1955, **19**, 167—176
4. Bond, J., *Loss Prev. Bull.*, 1995, **121**, 17

Readily formed from copper or its compounds and acetylene, it detonates on impact or heating above 100°C. If warmed in air or oxygen, it explodes on subsequent contact with acetylene [1]. Explosivity of the precipitate increases with acidity of the salt solutions, while the stability increases in the presence of reducing agents (formaldehyde, hydrazine, or hydroxylamine). The form with a metallic lustre was the most explosive acetylide made. Catalysts with the acetylide supported on a porous solid are fairly stable [2]. The ignition temperature of the pure red acetylide is 260—270°C. On exposure to air or oxygen, it is converted to black copper(II) acetylide, which ignites and explodes at 100°C [3]. It may be formed inadvertently in copper chemical plant; an account of such an incident and a procedure for making such equipment safe (treatment with warm 5% hydrogen peroxide, followed by sodium diethyldithiocarbamate of the same concentration) is reported [4].

See also Dicopper Butadiynide

See also Dicopper(I) 1,3,5,7,9,11,13,15,17,19,21,23,25,27,29,31,33,35,37,39,-tetracontaeicosayne-1,40-diide

Halogens

Mellor, 1946, Vol. 5, 852

Ignition occurs on contact with chlorine, bromine vapour or finely divided iodine.

Silver nitrate

Mellor, 1946, Vol. 5, 853

Contact with silver nitrate solution transforms copper(I) acetylide into a sensitive and explosive mixture of silver acetylide and silver.

Talc

Chambionnat, A., *Chem. Abs.*, 1951, **45**, 7791e

The effect of adding talc as an inert desensitiser upon the sensitivity of the acetylide has been studied.

Dicopper(I) 1,3,5,7,9,11,13,15,17,19,21,23,25,27,29,31,33,35,37,39,-tetracontaeicosayne-1,40-diide

Dicopper(I) butadiynide

See other METAL ACETYLIDES

0617. Copper(I) cyanide

[544-92-3] **$C_2Cu_2N_2$**

$$N\equiv C^{-} \quad Cu^{+}$$

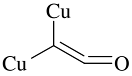
3-Methoxy-2-nitrobenzoyl chloride

See 3-Methoxy-2-nitrobenzoyl chloride

See other METAL CYANIDES

0618. Dicopper(I) ketenide

[41084-90-6] (ion) **C_2Cu_2O**



Blues, E. T. *et al., J. Chem. Soc., Chem. Comm.*, 1973, 921

The dry compound is mildly explosive.

See other HEAVY METAL DERIVATIVES

0619a. Copper(I) oxalate

[53421-36-6] **$C_2Cu_2O_4$**

CuOCO.CO.OCu

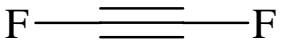
Sidgwick, 1950, 126

It explodes feebly on heating.

See other METAL OXALATES

0619b. Difluoroethyne (Difluoroacetylene)

[689-99-6] **C_2F_2**



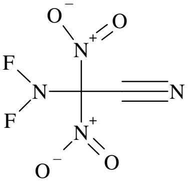
1. Feast, W. J., Personal communication, 1993
2. Bürger, H. *et al., J. Chem. Soc., Chem. Comm.*, 1991, 456

Like other substituted acetylenes, this is violently unstable. Attempts to prepare poly(difluoroacetylene) thence usually end in explosion [1]. Difluoroacetylene decomposes slowly even at liquid nitrogen temperatures [2].

See other HALOACETYLENE DERIVATIVES

0620. 2-(Difluoroamino)-2,2-dinitroacetonitrile

[180570-35-8] **$C_2F_2N_4O_4$**

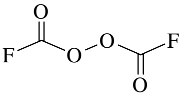


See 1,1-DINITRODIFLUORAMINES

See other *N*-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

0621. Bis(fluoroformyl) peroxide

[692-74-0] **$C_2F_2O_4$**

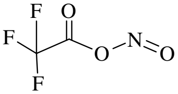


1. Talbot, R. L., *J. Org. Chem.*, 1968, **33**, 2095
2. Czerepinski, R. *et al., Inorg. Chem.*, 1968, **7**, 109
3. Russo, A. *et al., Inorg. Chem.*, 1995, **34**(24), 6221

Several explosions occurred during the preparation, which involves charging carbon monoxide into a mixture of fluorine and oxygen [1]. It has been known to decompose or explode at elevated temperatures, and all samples should be maintained below 30°C and well shielded [2]. It was found that the explosion risk depends upon the order in which the gases are introduced into the reactor, the sequence oxygen, fluorine and finally carbon monoxide was safest, with short pauses to allow each flow to become established [3].

See other DIACYL PEROXIDES

0622. Trifluoroacetyl nitrite
[667-29-8] **$C_2F_3NO_3$**

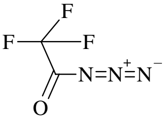


1. Taylor, C. W. *et al., J. Org. Chem.*, 1962, **27**, 1064
2. Gibbs, R. *et al., J. Chem. Soc., Perkin Trans. 2*, 1972, 1340
3. Banks, R. E. *et al., J. Chem. Soc. (C)*, 1956, 1350—1353
4. Banks, R. E. *et al., J. Chem. Soc., Perkin Trans. 1*, 1974, 2535

Though much more stable than acetyl nitrite even at 100°C, the vapour of trifluoroacetyl nitrite will explode at 160—200°C unless diluted with inert gas to below about 50 vol% concentration. Higher perfluorohomologues are more stable [1]. A detailed examination of the explosion parameters has been made [2]. This and higher polyfluoroacyl nitrites tend to explode above 140°C at ambient pressure, and handling of large quantities should be avoided [3], especially during pyrolysis [4].

See other ACYL NITRITES

0623. Trifluoroacetyl azide
[23292-52-6] **$C_2F_3N_3O$**



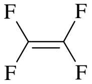
Sprenger, G. H. *et al., Inorg. Chem.*, 1973, **12**, 2891

It explodes on exposure to mechanical or thermal shock. Care is necessary during preparation to eliminate hydrogen chloride from the precursory acid chloride, to prevent formation of hydrogen azide.

See other ACYL AZIDES

†0624. Tetrafluoroethylene

[116-14-3] **C_2F_4**



1. Graham, D. P., *J. Org. Chem.*, 1966, **31**, 956
2. Muller, R. *et al., Paste u. Kaut.*, 1967, **14**, 903
3. Kirk Othmer, 1994, Vol. 11, 624; Ullmann, 1988, **A11**, 396
4. van Bramer, D. J., U.S. Pat. 5,866,727
5. Lietze, D., *Chem. Ing. Tech.*, 2001, **73**(4), 393

A terpene inhibitor is usually added to the monomer to prevent spontaneous polymerisation, and in its absence, the monomer will spontaneously explode at pressures above 2.7 bar. The inhibited monomer will explode if ignited [1]. Explosion under thermal initiation is now held to be a disproportionation, that to tetrafluoromethane and carbon gives 3.2 kJ/g, the same energy as black powder [3]. Liquid tetrafluoroethylene, being collected in a liquid nitrogen-cooled trap open to air, formed a peroxidic polymer which exploded [2]. Tetrafluoroethene is stabilised for transport or storage by admixture with considerable proportions of hexafluoropropene [4]. Explosion characteristics in long pipes at 23 bar pressure have been studied [5].

See other POLYMERISATION INCIDENTS

Air, Hexafluoropropene

Dixon, G. D., private comm., 1968

A mixture of the two monomers and air sealed in an ampoule formed a gummy peroxide during several weeks. The residue left after opening the ampoule exploded violently on warming.

See other POLYPEROXIDES

Chloroperoxytrifluoromethane

See Chloroperoxytrifluoromethane: Tetrafluoroethylene

Difluoromethylene dihypofluorite

See Difluoromethylene dihypofluorite: Haloalkenes

Dioxygen difluoride

See Dioxygen difluoride: Various materials

Iodine pentafluoride, Limonene

MCA Case History No. 1520

Accidental contamination of a tetrafluoroethylene gas supply system with iodine pentafluoride caused a violent explosion in the cylinders. Exothermic reaction of the limonene inhibitor with the contaminant present in the gas cylinders may have depleted the inhibitor and initiated explosive polymerisation.

See other POLYMERISATION INCIDENTS

Metal alkoxides

See Methyl trifluorovinyl ether

Oxygen

See Oxygen (Gas): Tetrafluoroethylene

Sulfur trioxide

See Sulfur trioxide: Tetrafluoroethylene

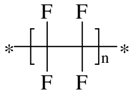
Triboron pentafluoride

See Triboron pentafluoride: Tetrafluoroethylene

See other HALOALKENES

0625. Poly(tetrafluoroethylene)

[9002-84-0] **$(C_2F_4)_n$**



Boron, or Magnesium, or Titanium

Shidlovskii, A. A. *et al., Chem. Abs.*, 1978, **88**, 193944

The combustion of compressed mixtures of the polymer with the finely powdered elements under nitrogen or argon has been studied, reactivity decreasing in the order B, Mg, Ti.

See also Aluminium: Polytetrafluoroethylene

Fluorine

See Fluorine: Polymeric materials

Metal hydrides

Andreev, B. M. *et al., Chem. Abs.*, 1987, **106**, 162978

In a study of thermal stability and hydrogen sorption characteristics of a series of sorbent tablets composed of hydride-forming metals dispersed in polymers under a 50% hydrogen in argon atmosphere, it was found that tablets of 80% palladium in PTFE, and 80% of 1:5 atom lanthanum—nickel alloy in PTFE could not be used above 247°C because of explosive decomposition of the PTFE.

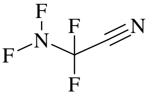
Oxygen

See FLUOROCARBONS

See related HALOALKANES

0626. (Difluoroamino)difluoroacetonitrile

[5131-88-4] **$C_2F_4N_2$**



Hydrazine

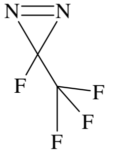
John, E. O. *et al., Inorg. Chem.*, 1988, **27**, 3100—3104

The major product of reaction of the nitrile with anhydrous hydrazine in THF at —196°, followed by slow warming to 25°C for 2 h, is 2-difluoroamino-2,2-difluoro-1-iminoethylhydrazine, $F_2NCF_2C(:NH)NHNH_2$, which is stable only in solution. Evaporation of solvent led on each occasion to mild explosions, caused by decomposition of the product with considerable gas evolution, for which a mechanism is suggested.

See other CYANO COMPOUNDS, DIFLUOROAMINO COMPOUNDS, GAS EVOLUTION INCIDENTS

0627a. 3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine

[117113-32-0] **$C_2F_4N_2$**



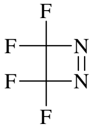
Dailey, W. P., *Tetrahedron Lett.*, 1987, **28**, 5801—5804

As it is potentially explosive in neat liquid or solid forms, it is best handled in solution.

See other DIAZIRINES, *N*-HALOGEN COMPOUNDS

0627b. 3,3,4,4-Tetrafluoro-3,4-dihydro-1,2-diazete

[694-60-0] **$C_2F_4N_2$**



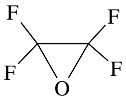
Emeléus, H. J. *et al., J. Chem. Soc.* 1962, 3276

A gas, the major product of fluorination of cyanogen with silver difluoride was assigned this, mechanistically improbable, structure. Usually decomposing above 150°C, it twice detonated spontaneously at room temperature (initial pressure not stated).

See N-HALOGEN COMPOUNDS

0628. Tetrafluorooxirane (Tetrafluoroethylene oxide)

[694-17-7] **C_2F_4O**



Preparative hazard

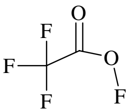
Eleuterio, H. S., *J. Macromol. Sci., Chem.*, 1972, **6**, 1027

Formation from tetrafluoroethylene and oxygen may be explosive. It rearranges to trifluoroacetyl fluoride above its b.p., —63.5°C.

See Oxygen: Tetrafluoroethylene
See other 1,2-EPOXIDES

0629. Trifluoroacetyl hypofluorite

[359-46-6] **$C_2F_4O_2$**



Alone, or Potassium iodide, Water

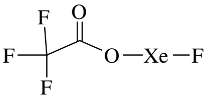
Cady, G. H. *et al., J. Amer. Chem. Soc.*, 1953, **75**, 2501—2502

The gas explodes on sparking and often during preparation or distillation. Unless much diluted with nitrogen, it explodes on contact with aqueous potassium iodide.

See other ACYL HYPOHALITES

0630. Xenon(II) fluoride trifluoroacetate

[25710-89-8] **$C_2F_4O_2Xe$**



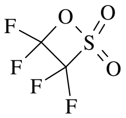
Jha. N. K., *RIC Rev.*, 1971, **4**, 157

It explodes on thermal or mechanical shock.

See other XENON COMPOUNDS

0631. Tetrafluorooxathietane-2,2-dioxide (Tetrafluoroethane sultone)

[697-18-7] **$C_2F_4O_3S$**

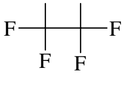


Preparative hazard

See Sulfur trioxide: Tetrafluoroethylene

0632. Pentafluoroethyllithium (Perfluoroethyllithium)

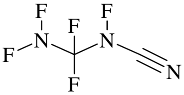
[91935-83-0] **C_2F_5Li**



Roddick, D. M., *Chem. Eng. News*, 1997, **75**(40), 6

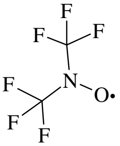
This reagent, prepared in situ from butyllithium and chloropentafluoroethane as an ether solution, has several times decomposed violently on addition of a few drops of a chlorophosphine. This is attributed to running the preparation too cool (< —90°C), so that it had not proceeded. However:
See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

0633. Perfluoro-*N*-cyanodiaminomethane
[16408-94-9] **$C_2F_5N_3$**



See Fluorine: Sodium dicyanamide
See other CYANO COMPOUNDS, DIFLUOROAMINO COMPOUNDS

0634. Bis(trifluoromethyl) nitroxide
[2154-71-4] **C_2F_6NO**



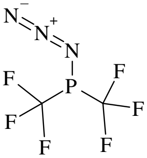
Benzoyl azide

Banks, R. E. *et al., J. Chem. Soc., Perkin Trans. 1*, 1981, 455—456
Interaction on warming from —196°C in absence of solvent led to a violent explosion.

Platinum hexafluoride

See Platinum hexafluoride: Bis(trifluoromethyl) nitroxide
See other N—O COMPOUNDS

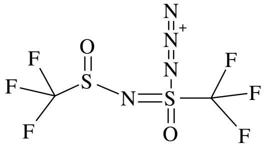
0635. Bis(trifluoromethyl)phosphorus(III) azide
[1479-48-7] **$C_2F_6N_3P$**



1. Allcock, H. R., *Chem. Eng. News*, 1968, **46**(18), 70
2. Tesi, G. *et al., Proc. Chem. Soc.*, 1960, 219

Explosive, but stable if stored cold [1]. Previously it was found to be unpredictably unstable, violent explosions having occurred even at —196°C [2].
See other NON-METAL AZIDES

0636. *N*-(Trifluoromethylsulfinyl)trifluoromethylimidosulfinyl azide
[81341-46-0] **$C_2F_6N_4O_2S_2$**

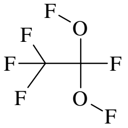


Bechtold, T. *et al., J. Fluorine Chem.*, 1981—2, **19**, 385

An explosive liquid.

See other ACYL AZIDES, N—S COMPOUNDS

0637. 1,1-Bis(fluorooxy)tetrafluoroethane
[16329-92-3] **$C_2F_6O_2$**

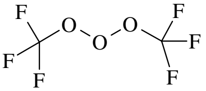


1. Thompson, P. G. *et al., J. Amer. Chem. Soc.*, 1967, **89**, 2203
2. Sekiya, A. *et al., Inorg. Chem.*, 1980, **19**, 1329—1330

Though reported to be stable up to 200°C in metal [1], samples in glass at 22°C exploded during vaporisation at ambient pressure, or when a sealed tube was broken. Higher homologues are less stable [2].

See other BIS(FLUOROOXY)PERHALOALKANES, GLASS INCIDENTS

0638. Bis(trifluoromethyl)trioxide
[1718-18-9] **$C_2F_6O_3$**

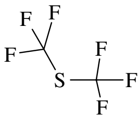


Gobbato, K. I. *et al.*, *Angew. Chem. (Int.)*. 1995, **34** (20), 2244

This unstable gas (b.p. —16°C) has never been reported as exploding, possibly because experimenters have always exercised the greatest caution. It is recommended that this continue. As well as being thermodynamically unstable, the immediate decomposition products being trifluoromethyl peroxide and oxygen, it should also be a strong oxidant and therefore a greater danger in presence of combustible organics.

See ORGANIC PEROXIDES

0639. Bis(trifluoromethyl) sulfide
[371-78-8] **C_2F_6S**



Chlorine fluorides

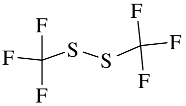
Sprenger, G. H. *et al., J. Fluorine Chem.*, 1976, **7**, 335

In the preparation of bis(trifluoromethyl)sulfur difluoride, explosions have occurred when chlorine mono- or tri-fluorides were treated with 2—3 mmol of the sulfide in absence of solvent. Because chlorine trifluoride is known to deprotonate solvents with formation of explosive carbene species, only fully halogenated solvents are suitable as diluents.

See other ALKYLNON-METALS

0640a. Bis(trifluoromethyl) disulfide

[372-64-5] **$C_2F_6S_2$**



Chlorine fluorides

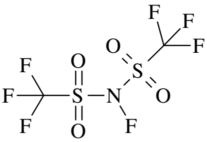
Sprenger, G. H. *et al., J. Fluorine Chem.*, 1976, *57*, 335

In the preparation of bis(trifluoromethyl)sulfur difluoride, the presence of fully halogenated solvents is essential to prevent explosion during treatment of the disulfide with chlorine mono- or tri-fluoride.

See related ALKYLNON-METALS

0640b. *N*-Fluorobis(trifluoromethanesulfonyl)imide (*N*,1,1,1-Tetrafluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide)

[108388-06-3] **$C_2F_7NO_4S_2$**



Preparative hazard

Banks, R. E. *et al., J. Fluor. Chem.*, 2001, **112**(2), 271

On three occasions explosive products, not conclusively identified, were obtained when preparing this by fluorination of the lithium salt of trifluoromethanesulfonamide.

N,N-Difluoromethanesulfonamide

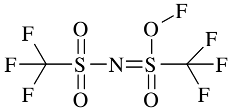
See N-(Trifluoromethanesulfonyl)trifluoromethanesulfonimidyl hypofluorite

See also N-HALOGEN COMPOUNDS

See also N-HALOIMIDES

0640c. *N*-(Trifluoromethanesulfonyl)trifluoromethanesulfonimidyl hypofluorite (1,1,1-Trifluoro-*N*-[(trifluormethyl)sulfonyl]methanesulfonimidic acid, anhydride with hypofluorous acid)

[410521-74-3] **$C_2F_7NO_4S_2$**



Banks, R. E. *et al., J. Fluor. Chem.*, 2001, **112**(2), 271

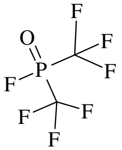
This compound, of high calculated energy, was advanced as one possible cause of explosions experienced when preparing the *N*-fluorosulfonimide isomer, (next above).

See also N,N-Difluoromethanesulfonamide

See other HYPOHALITES

0641. Fluorobis(trifluoromethyl)phosphine oxide

[34005-83-9] **C_2F_7OP**



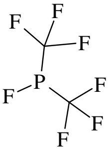
Preparative hazard

See Fluorobis(trifluoromethyl)phosphine, next below

See related ALKYLHALOPHOSPHINES

0642. Fluorobis(trifluoromethyl)phosphine

[1426-40-0] **C_2F_7P**



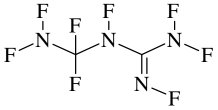
Mahler, W., *Inorg. Chem.*, 1979, **18**, 352

Admission of air to effect oxidation to the phosphine oxide must be slow to prevent ignition.

See other ALKYLHALOPHOSPHINES

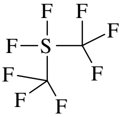
0643. Perfluoro-1-aminomethylguanidine

[16408-93-8] **$C_2F_8N_4$**



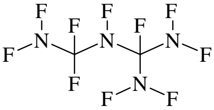
See Fluorine: Cyanoguanidine
See other N,N,N′-TRIFLUOROAMIDINES

0644. Bis(trifluoromethyl)sulfur difluoride
[30341-38-9] **C_2F_8S**



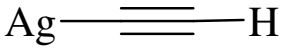
Preparative hazard
Bis(trifluoromethyl) disulfide: Chlorine fluorides
See Bis(trifluoromethyl) sulfide: Chlorine fluorides
See related ALKYLNON-METAL HALIDES

0645. *C,N*-Perfluoro-*N*-aminomethyltriaminomethane
[16408-92-7] **$C_2F_{10}N_4$**



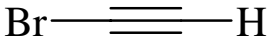
See Fluorine: Cyanoguanidine
See other DIFLUOROAMINO COMPOUNDS

0646. Monosilver acetylide
[13092-75-6] **C_2HAg**



Anon., *Chem. Trade J.*, 1966, **158**, 153
A poorly stoppered dropping bottle of silver nitrate solution absorbed sufficient acetylene from the atmosphere in an acetylene plant laboratory to block the dropping tube. A violent detonation occurred on moving the dropping tube.
See Silver nitrate: Acetylene
See other METAL ACETYLIDES

0647. Bromoacetylene
[593-61-3] **C_2HBr**



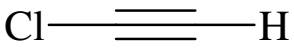
1. Tanaka, R. *et al., J. Org. Chem.*, 1971, **36**, 3856
2. Hucknall, D. J. *et al., Chem. & Ind.*, 1972, 116

It is dangerous and may burn or explode in contact with air, even when solid at —196°C [1]. Procedures for safe generation, transfer and storage, all under nitrogen, are described [2].

See other HALOACETYLENE DERIVATIVES

0648. Chloroacetylene

[593-63-5] **C_2HCl**



Tanaka, R. *et al., J. Org. Chem.*, 1971, **36**, 3856

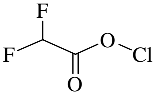
It is notably endothermic (ΔH_f° (g) +213 kJ/mol, 3.52 kJ/g). Chloroacetylene will burn and may explode in contact with air, and its greater volatility makes it more dangerous than bromoacetylene. Procedures for safe generation, handling and storage, all under nitrogen, are described.

See Trichloroethylene: Alkali

See other ENDOTHERMIC COMPOUNDS, HALOACETYLENE DERIVATIVES

0649. Difluoroacetyl hypochlorite

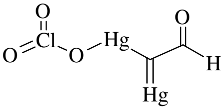
[71359-63-2] **$C_2HClF_2O_2$**



See entry ACYL HYPOHALITES (reference 1)

0650. Chloratomercurio(formyl)methylenemercury(II)

[ ] **$C_2HClHg_2O_4$**



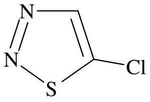
Whitmore, 1921, 154

An extremely sensitive crystalline solid, which explodes on shaking with its crystallisation liquor, or upon gentle mixing when dry with copper oxide (for analysis).

See other MERCURY COMPOUNDS

0651. 5-Chloro-1,2,3-thiadiazole

[4113-57-9] **C_2HClN_2S**



1. Yoshida, T. et al., *Safety of Reactive Chemicals & Pyrotechnics*, p29, Amsterdam, Elsevier, 1995
2. Ouchi, H. *et al., Kogyo Kayaku*, 1984, **45**, 73 (*Chem. Abs.,* 1985, **102**, 187475)

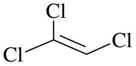
Two industrial-scale accidents which involved explosive decomposition of this intermediate caused great damage. The compound has considerable explosive potential (about 80% that of TNT) for, though it lacks oxygen in its structure, it is of rather low oxygen balance [1]. A comprehensive examination using several hazard evaluation techniques revealed it as an extremely dangerous compound. DSC and the drop-hammer test on the solid do not indicate hazard potential, but ARC at 126°C under adiabatic conditions give a corrected time-to-explosion of 40 min. The impact-sensitivity was determined as 2 kgcm [2].

See entry OXYGEN BALANCE

See other N—S COMPOUNDS

†0652. Trichloroethylene

[79-01-6] **C_2HCl_3**



(*MCA SD-14*, 1956); *NSC 389*, 1979; *HCS 1980*, 919; *RSC Lab. Hazard Data Sheet No. 13*, 1983

1. Author’s comments, 1988
2. Santon, R. C. *et al., Proc. 6th Intl. Sympos. Loss Prev. Safety Prom. Proc. Ind.*, 1989, Oslo, Norweg. Soc C. Eng.

Though usually considered to be non-flammable in use, it has unusually wide flammability limits, and with an AIT of 410°C it can be ignited by a flame or other intense source. The Data Sheet is devoted to all aspects of laboratory use [1]. The limits of flammability have been determined more accurately as 8.5 vol%/25°C to 14.5%/35°, widening to 6.0—47% at 150°C. Intermediate values are also given [2].

See FLASH POINTS (reference 19)

Alkali

1. Fabian, F., private comm., 1960
2. *ABCM Quart. Safety Summ.*, 1956, **27**, 17
3. Anon., *Jahresber.*, 1978, 70

An emulsion, formed during extraction of a strongly alkaline liquor with trichloroethylene, decomposed with evolution of the spontaneously flammable gas, dichloroacetylene [1]. This reaction could also occur if alkaline metal-stripping preparations were used in conjunction with trichloroethylene degreasing preparations, some of which also contain amines as inhibitors, which could also cause the same reaction [2]. Apparently accidental contact of the solvent with potassium hydroxide solution led to generation of flames in the charging port of a stirred reactor [3].

See Tetrachloroethylene: Sodium hydroxide

Aluminium

See Aluminium: Halocarbons

Epoxides

Dobinson, B. *et al., Chem. & Ind.*, 1972, 214

1-Chloro-2,3-epoxypropane, the mono- and di-2,3-epoxypropyl ethers of 1,4-butanediol, and 2,2-bis[4(2′,3′-epoxypropoxy)phenyl]propane can, in presence of catalytic quantities of halide ions, cause dehydrochlorination of trichloroethylene to dichloroacetylene, which causes minor explosions when the mixture is boiled under reflux. A mechanism is discussed.

See Alkali, above

Metals

See Aluminium: Halocarbons
Barium: Halocarbons
Beryllium: Halocarbons
Lithium: Halocarbons
Magnesium: Halocarbons
Titanium: Halocarbons

Oxidants

See Dinitrogen tetraoxide: Halocarbons
Oxygen (Gas): Halocarbons
Oxygen (Liquid): Halocarbons
Perchloric acid: Trichloroethylene

Water

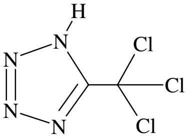
Brade, C., *Chem. Tech.* (Berlin), 1952, **4**, 506—507

A violent explosion occurred during routine recovery of wet trichloroethylene by distillation at ambient pressure. This was attributed to hydrolytic formation of hydrochloric acid and concentration of the latter, leading to corrosion and blocking of the vent line which caused pressure development and a consequential increase in distillation temperature of the vessel contents. The corrosion products may have catalysed the exothermic decomposition reaction which led to explosion. The vessel contained much carbonised residue.

See other CORROSION INCIDENTS, HALOALKENES

0653. 5-Trichloromethyltetrazole

[2925-21-5] **$C_2HCl_3N_4$**



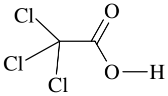
1. Beck, W. *et al., Chem. Eng. News*, 1984, **62**(10), 39
2. Finnegan, W. G. *et al., J. Amer. Chem. Soc.*, 1958, **80**, 3908

3. Howe, R. K. *et al., Chem. Eng. News*, 1983, **61**(3), 4
4. Burke, L. A., *Chem. Eng. News*, 1983, **61**(17), 2

The later publication [1] reveals that the title compound is in fact a relatively stable compound. The previously attempted preparation of the then unknown compound from trichloroacetonitrile, sodium azide and ammonium chloride (0.14: 0.42: 0.2 mol) by an analogous established method [2], but at lower initial temperature because of the exothermic reaction, gave, after vacuum evaporation of solvent, an oily product. When sampled with a pipette, this evolved gas and then exploded violently. It was thought that an azidomethyltetrazole may have been formed by displacement of chloro-substituent(s) by the excess azide employed [3]. An alternative hypothesis which involved isomerisation of the title compound to the open chain azidoazomethine [4] was discounted, because no trace of this could be detected [1].

See other TETRAZOLES

0654. Trichloroacetic acid
[76-03-9] **$C_2HCl_3O_2$**



Copper, Dimethyl sulfoxide

See Dimethyl sulfoxide: Copper, etc.

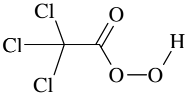
Methanol, Water

1. Mabbott, D. J., Personal communication, 1997
2. Ullmann, 1986, Vol. A6, 545.
3. Merck Index, 1989, 1515

A bottle labelled as 12% acid in aqueous methanol, and probably two years forgotten, exploded in storage, breaking adjacent bottles [1]. Trichloracetic acid is known to be more unstable, with respect to carbon dioxide and chloroform, in aqueous solution than pure. The reaction usually requires either heat or base catalysis [2]. Storage of trichloroacetic acid at less than 30% concentration is not advised [3]. Hydrolysis of the trichlorogroup is also conceivable, which would yield intermediate oxalyl monochloride, which habitually breaks down to give carbon monoxide, dioxide and hydrogen chloride.

See other ORGANIC ACIDS

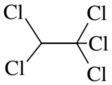
0655. Trichloroperoxyacetic acid
[7796-16-9] **$C_2HCl_3O_3$**



Swern, D., *Chem. Rev.*, 1945, **45**, 10

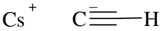
Very unstable, forming mainly the toxic gaseous products phosgene, chlorine, carbon monoxide and hydrogen chloride.
See other GAS EVOLUTION INCIDENTS, PEROXYACIDS

0656. Pentachloroethane
[76-01-7] **C_2HCl_5**



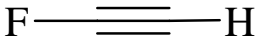
Potassium
See Potassium: Halocarbons
See other HALOALKANES

0657. Monocaesium acetylide
[30180-52-0] **C_2HCs**



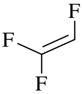
Mellor, 1946, Vol. 5, 849—850
It reacts similarly to the dicaesium compound.
See Caesium acetylide
See other METAL ACETYLIDES

0658. Fluoroacetylene
[2713-09-9] **C_2HF**



Alone, or Bromine
Middleton, W. J. *et al., J. Amer. Chem. Soc.*, 1959, **81**, 803—804
It is notably endothermic (ΔH_f° (g) $+125$ kJ/mol, 2.84 kJ/g), and liquid fluoroacetylene is treacherously explosive close to its b.p., —80°C. The gas does not ignite in air and is not explosive. Ignition occurred in contact with a solution of bromine in carbon tetrachloride. The mercury and silver salts were stable to impact, but the latter exploded on heating, whereas the former decomposed violently.
See other ENDOTHERMIC COMPOUNDS, HALOACETYLENE DERIVATIVES

†0659. Trifluoroethylene
[359-11-5] **C_2HF_3**



Hulbert, J. D. *et al., Chem. Eng. News* 1997, **75**(51), 6

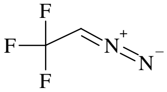
Trifluoroethene at pressures above 14 bar, and possibly below, deflagrates with tenfold pressure rises when initiated by an exploding wire. The tests were on air-free and inhibited commercial material.

See also Ethylene, Tetrafluoroethylene

See other HALOALKENES

0660. 2,2,2-Trifluorodiazoethane

[371-67-5] **$C_2HF_3N_2$**



Fields, R. *et al., J. Fluorine Chem.*, 1979, **13**, 154

The stabilising effect of the trifluoromethyl group is insufficient to prevent explosions, either of the compound itself, or of unstable reaction intermediates formed at low temperatures, especially in absence of solvent. Energy released on explosion is estimated at 50—100% TNT eqivalent.

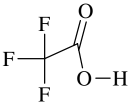
Ozone

See Ozone: Trifluoroethylene

See other DIAZO COMPOUNDS

0661. Trifluoroacetic acid

[76-05-1] **$C_2HF_3O_2$**



HCS 1980, 935

Unlike the chloro-analogue this acid is not reported as decarboxylating and has been proclaimed a perdurable environmental hazard by ozone-warriors and their kin. Although the activation energy will be higher, thermodynamically decarboxylation is very much favoured and may have contributed to some of the incidents below.

Aromatic hydrocarbons, Hydrogen peroxide

See Hydrogen peroxide: Aromatic hydrocarbons, Trifluoroacetic acid

Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Fluoroamides

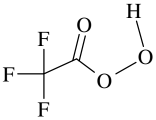
See other ORGANIC ACIDS

Sodium tetrahydroborate

See Sodium tetrahydroborate, Trifluoroacetic acid

0662. Peroxytrifluoroacetic acid

[359-48-8] **$C_2HF_3O_3$**



Sundberg, R. J. *et al., J. Org. Chem.*, 1968, **33**, 4098

This extremely powerful oxidant must be handled and used with great care.

4-Iodo-3,5-dimethylisoxazole

Plepys, R. A. *et al.*, US Pat. 3 896 140, 1975

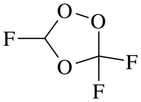
Interaction to produce 3,5-dimethyl-4-bis(trifluoroacetoxy)iodoisoxazole yields a detonable by-product, believed to be iodine pentaoxide contaminated with organic material.

See Iodine(V) oxide: Non-metals

See other OXIDANTS, PEROXYACIDS

0663. 3,3,5-Trifluoro-1,2,4-trioxolane (Trifluoroethylene ozonide)

[86013-87-8] **$C_2HF_3O_3$**



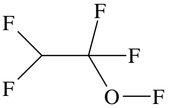
Explosive.

See Ozone: Trifluoroethylene

See other OZONIDES

0664. 1,1,2,2-Tetrafluoro-1-(fluoroxy)ethane (1,1,2,2-Tetrafluoroethyl hypofluorite)

[ ] **C_2HF_5O**



Randolph, B. B. *et al., J. Fluorine Chem.*, 1993, **64**(1-2), 129

The hypofluorite exploded on attempted purification. A variety of related compounds were also unstable, if not explosive.

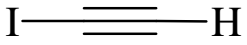
See other HYPOHALITES

0665. Poly(dimercuryimmonium acetylide)

[ ] **$(C_2HHg_2N)_n$**

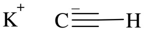
Sorbe, 1968, 97
Highly explosive.
See other POLY(DIMERCURYIMMONIUM) COMPOUNDS

0666. Iodoacetylene
[14545-08-5] **C_2HI**



Sorbe, 1968, 65
It explodes above 85°C.
See other HALOACETYLENE DERIVATIVES

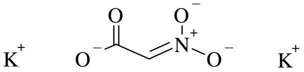
0667. Monopotassium acetylide
[1111-63-3] **C_2HK**



Chlorine
Mellor, 1946, Vol. 5, 849
It ignites in chlorine.

Non-metal oxides
Mellor, 1946, Vol. 5, 849
Interaction with sulfur dioxide at ambient temperature, or with carbon dioxide on warming, causes incandescence.
See other METAL ACETYLIDES

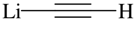
0668. Dipotassium *aci*-nitroacetate
[19419-98-8] **$C_2HK_2NO_4$**



Water
1. Lyttle, D. A., *Chem. Eng. News*, 1949, **27**, 1473
2. Whitmore, F. C., *Org. Synth.*, 1941, Coll. Vol. 1, 401

An inhomogeneous mixture of the dry salt with a little water exploded violently after 30 min [1]. This was probably owing to exothermic decarboxylation generating the *aci*-salt of nitromethane, which is explosively unstable. The decomposition of sodium nitroacetate proceeds exothermically above 80°C [2].
See other aci-NITRO SALTS

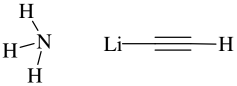
0669. Monolithium acetylide
[1111-64-4] **C_2HLi**



Mellor, 1946, Vol. 5, 849
It reacts similarly to the dilithium salt.
See Lithium acetylide
See other METAL ACETYLIDES

0670. Monolithium acetylide—ammonia

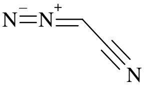
[ ] **$C_2HLi.H_3N$**



Gases, or Water
Mellor, 1946, Vol. 5, 849
The complex ignites in contact with carbon dioxide, sulfur dioxide, chlorine or water.
See related METAL ACETYLIDES

0671. Diazoacetonitrile

[13138-21-1] **C_2HN_3**

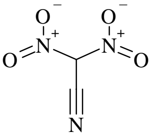


1. Phillips, D. D. *et al., J. Amer. Chem. Soc.*, 1956, **78**, 5452
2. *MCA Case History No. 2169*
3. Roelants, F. *et al., Tetrahedron*, 1978, **34**, 2231
4. Author's comments

Removal of a rubber stopper from a flask of a concentrated solution in methylene chloride initiated an explosion, probably through friction on solvent-free material between the flask neck and bung. Handling only in dilute solution is recommended [1]. An explosion also occurred during operation of the glass stopcock of a dropping funnel while 20 ml of the apparently undiluted nitrile was being added to a reaction mixture [2]. All attempts to isolate the nitrile from its solutions in chlorinated solvents caused explosions [3]. By inference from the thermodynamic properties of diazomethane and acetonitrile, diazoacetonitrile should be strongly endothermic, with heat of formation exceeding 200 kJ/mol, 3 kJ/g [4].
See other DIAZO COMPOUNDS, FRICTIONAL INITIATION INCIDENTS, GLASS INCIDENTS

0672. Dinitroacetonitrile

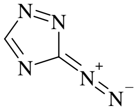
[921-22-2] **$C_2HN_3O_4$**



See entry POLYNITROALKYL COMPOUNDS

0673. 3-Diazo-3*H*-1,2,4-triazole

[64781-78-8] **C_2HN_5**



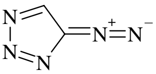
The precursory 1,2,4-triazole-3-diazonium nitrate is extremely unstable, even in ice-cold aqueous solution, and no attempt was made to isolate the title diazo compound from its solution, prepared by cautious treatment of the cold diazonium nitrate solution with dilute aqueous potassium hydroxide with cooling.

See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

0674. 4-Diazo-1,2,3-triazole

[85807-68-7] **C_2HN_5**

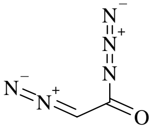


See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

0675. Diazoacetyl azide

[19932-64-0] **C_2HN_5O**



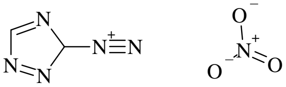
Neunhöffer, G. *et al., Ann.*, 1968, **713**, 97—98

The material may be distilled cautiously at 20—21°/0.27 mbar but is preferably used in solution as prepared. Either the solid (below 7°C) or the liquid explodes with great violence on impact or friction.

See other ACYL AZIDES, DIAZO COMPOUNDS

0676. 1,2,4-Triazole-3-diazonium nitrate

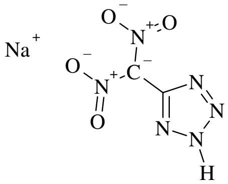
[59104-93-7] **$C_2HN_6O_3$**



Magee, H. L. *et al., J. Org. Chem.*, 1987, **52**, 5547

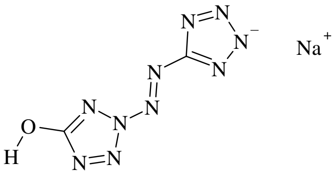
The diazonium nitrate is extremely unstable and may only be prepared as an aqueous solution of limited life at below 0°C.
See other DIAZONIUM SALTS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

0677. Sodium 5-(dinitromethyl)tetrazolide
[2783-96-2] **$C_2HN_6NaO_4$**



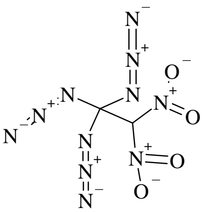
Einberg, F., *J. Org. Chem.*, 1964, **29**, 2021
It explodes violently at the m.p., 160°C, and may be an *aci*-nitro salt.
See other POLYNITROALKYL COMPOUNDS, TETRAZOLES

0678. Sodium 5(5′-hydroxytetrazol-3′-ylazo)tetrazolide
[ ] **$C_2HN_{10}NaO$**



Thiele, J. *et al., Ann.*, 1893, **273**, 150
The salt explodes very violently on heating.
See other AZO COMPOUNDS, TETRAZOLES

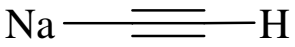
0679. 1,1,1-Triazidodinitroethane
[56522-42-0] **$C_2HN_{11}O_4$**



Frankel, M. B. *et al.*, UK Pat. Appl. 2 123 829, 1984
An energetic compound (with 63% N and of low oxygen balance).
See other ORGANIC AZIDES, POLYNITROALKYL COMPOUNDS

0680. Monosodium acetylide

[1066-26-8] **C_2HNa**



1. Mellor, 1946, Vol. 5, 849
2. Greenlee, K. W., *Inorg. Synth.*, 1947, **2**, 81
3. Houben-Weyl, Vol. 13.1, 280

It reacts similarly to the disodium salt [1]. If heated to 150°C, it decomposes extensively, evolving gas which ignites in air owing to presence of pyrophoric carbon. The residual carbon is also highly reactive [2]. The dry powder (from solution in liquid ammonia) may ignite if exposed to air as an extended layer, e.g. on filter paper [3].

See Sodium acetylide

See other METAL ACETYLIDES

0681. Monorubidium acetylide

[20720-71-2] **C_2HRb**

Mellor, 1946, Vol. 5, 849

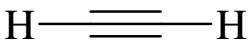
It reacts similarly to the dirubidium salt.

See Rubidium acetylide

See other METAL ACETYLIDES

†0682. Acetylene (Ethyne)

[74-86-2] **C_2H_2**



(*MCA SD-7*, 1957); *NSC 494*, 1982; *FPA H6*, 1972; *HCS 1980*, 110, 111

1. Mayes, H. A., *Chem. Engr.*, 1965, (185), 25
2. Nedwick, J. J., *Ind. Eng. Chem., Proc. Des. Dev.*, 1962, **1**, 137; Tedeschi, R. J. *et al.*, ibid., 1968, **7**, 303
3. Miller, 1965, Vol. 1, 506
4. Kirk-Othmer, 1963, Vol. 1, 195—202
5. Rimarski, W., *Angew. Chem.*, 1929, **42**, 933
6. Foote, C. S., private comm., 1965
7. Sutherland, M. E. *et al., Chem. Eng. Progr.*, 1973, **69**(4), 48—51
8. Williams, A. *et al., Chem. Rev.*, 1970, **70**, 270—271
9. Menge, R. *et al., Brandschutz, Explosionschutz*, 1987, **16**, 109
10. Yantovskii, S. A., *Chem. Abs.*, 1964, **61**, 13117f
11. Landesman, Ya. M. *et al., Chem. Abs.*, 1974, **81**, 151352
12. Glikin, M. A. *et al., Chem. Abs.*, 1975, **83**, 100289
13. Savitskaya, L. M. *et al., Chem. Abs.*, 1978, **88**, 157743

14. Viallon, J., *Loss Prev. Safety Prom. Proc. Ind.*, 121—122, Frankfurt, Dechema, 1978
15. Lietze, D. *et al., Chem. Ing. Tech.*, 1978, **50**, 808—809 (summary of 21 page paper)
16. Code of Practice for Acetylene Pipelines, Paris, Euro. Comm. Indust. Gases, 1978
17. Grosse-Wortmann, H. *et al., Chem. Ing. Tech.*, 1981, **53**, 461—463
18. Lietze, D., *Chem. Abs.*, 1986, **105**, 48048
19. Ashmore, F. S. *et al., Fire Prev.*, 1987, (204), 37—39; *Loss Prev. Bull.*, 1988, (080), 15—18
20. Marcks, G., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 623—649, Heidelberg, ISSA, 1987
21. Dorfinger, S., *ibid.*, 653—663
22. Schildberg, H. P. *et al., Chem. Ing. Tech.*, 1994, **66**(10), 1389

The extremely endothermic gas (ΔH_f° (g) +226.7 kJ/mol, 8.72 kJ/g) may decompose explosively in absence of air. Addition of up to 30% of miscible diluent did not sufficiently desensitise explosive liquid acetylene to permit of its transportation. The solid has similar properties [1]. However, safe techniques for the use of liquid acetylene in reaction systems at pressures up to 270 bar have been described [2]. Solid acetylene in admixture with liquid nitrogen at —181°C is sensitised by presence of grit (carborundum) and may readily explode on impact [3]. The hazards of preparing and using acetylene have been adequately described, including many reports of explosions in acetylene generators and distribution systems (formerly including domestic lighting installations) where faulty pressure control has allowed pressures to approach 1.4 bar, when explosion occurs in presence of moisture [3,4,5]. A glass flask which had contained acetylene was left open to atmosphere for a week, and then briefly purged with air. It still contained enough acetylene to form an explosive mixture [6]. The explosive decomposition of acetylene in absence of air readily escalates to detonation in tubular vessels. This type of explosive decomposition has been experienced in a 7 mile acetylene pipeline system [7].

In a review on combustion and oxidation of acetylene, the factors affecting spontaneous ignition at low temperatures are discussed [8]. The autoignition temperature may be as low as 85°C when mixed with 1—2% of nitric oxide (NO) [9]. The explosive decomposition of acetylene and conditions necessary for spontaneous ignition to occur have been reviewed [10,11,12]. Use of C_1—C_4 alcohols, C_3—C_4 ketones, C_1 and C_4 acids and C_3—C_4 diols or hydrocarbons to retard explosive decomposition was studied comparatively. The retardation mechanism involves thermal and chemical factors, related to heat content of diluent and to structure, respectively. Practical systems are detailed [13]. Acetylene at 170°C is somewhat stabilised by presence of acetic acid [14]. It is destabilised by potassium hydroxide [22]. The course of explosive decomposition of the gas in pipelines has been studied experimentally [15]. The EU Code of Practice divides pipeline systems into 3 ‘working ranges’, depending on internal pressure and diameter of the pipe, and specifies suitable design and construction criteria for each range [16]. The relationship between initiation energy and decomposition has been studied [17]. The explosibility of acetylene, alone or admixed with air, hydrogen or ethylene has been reviewed, including boundary limits for deflagration/detonation transformation [18].

Accidental local heating to 185°C or above of part of the wall (as little as 6 sq. cm may be enough) of a cylinder containing acetylene may lead to the development of an extremely dangerous situation. At this temperature, exothermic and self-sustaining decomposition, or polymerisation, of (endothermic) acetylene may set in, and if not stopped by rapid and effective cooling (large volume water spray), the cylinder may explode without warning. Flame flash-back into a cylinder from a wrongly adjusted and/or damaged welding or cutting torch can cause the same effect. Methods of identifying such unstable cylinders and of emergency control are detailed [19]. The hazards associated with installations of banks of acetylene cylinders connected to a high-pressure manifold are discussed [20], and a detailed account of an accident involving explosion of two such overheated cylinders is given [21].
See Magnesium: Barium carbonate, Water

Bleaching powder
See Oxidants, below

Cobalt MRH 8.70/tr.
Mellor, 1942, Vol. 14, 513
Finely divided (pyrophoric) cobalt decomposes acetylene on contact, becoming incandescent.

Copper MRH 8.70/tr.
Anon., *ABCM Quart. Safety Summ.*, 1946, **17**, 24
Rubber-covered electric cable, used as a makeshift handle in the effluent pit of an acetylene plant, formed copper acetylide with residual acetylene and the former detonated when disturbed and initiated explosion of the latter. All heavy metals must be rigorously excluded from locations where acetylene may be present.
See METAL ACETYLIDES

Copper(I) acetylide MRH 8.70/tr.
See Dicopper(I) acetylide

Dinitrogen oxide
See ATOMIC ABSORPTION SPECTROSCOPY

Ethylene, Hydrogen
See Hydrogen (Gas): Acetylene, Ethylene

Gaseous additives
1. Konovalov, E. N. *et al., Chem. Abs.*, 1975, **82**, 111548
2. Detz, C. M., *Combust. Flame*, 1979, **34**, 187—193; US Pat. 4 161 495, 1979

Addition of 0.3—3.5 wt% of propane or butane reduces the explosion hazards of acetylene—air mixtures [1]. Out of 10 gaseous additives tested for effect on the threshold temperature for initiation of explosive decomposition of acetylene by a heated wire at 2—22 bar, nitrogen oxide, hydrogen bromide, hydrogen chloride, hydrogen iodide and vinyl bromide showed stabilising effects, and sulfur dioxide a mild destabilising effect. The patent specifies use of one or more of these radical scavenging agents at levels of 0.5—10% [2].

Halogens MRH Chlorine or Iodine 8.70/tr.

1. Muir, G. D., private comm., 1968
2. von Schwartz, 1918, 142, 321
3. *MCA SD-7*, 1957
4. Humphreys, V., *Chem. & Ind.*, 1971, 681—682
5. Sokolova, E. I. *et al., Chem. Abs.*, 1970, **72**, 71120
6. Davenport, A. P., *School Sci. Rev.*, 1973, **55**(191), 332
7. Long, G. C., *Spectrum* (Pretoria), 1980, **18**, 30
8. Nolan, 1983, Case History 22
9. Nolan, 1983, Case History 23

Tetrabromoethane is made by passing acetylene into bromine in carbon tetrachloride at reflux. The rate of reaction falls off rapidly below reflux temperature, and if the rate of addition of acetylene is insufficient to maintain the temperature, high concentrations of unreacted acetylene build up, with the possibility of a violent delayed reaction [1]. In absence of a diluent, reaction may be explosive [2]. Mixtures of acetylene and chlorine may explode upon initiation by sunlight or other UV source, or at high temperature, sometimes very violently [2]. Interaction with fluorine is very violent [3] and with iodine possibly explosive [2]. Dilution of equimolar mixtures of chlorine and acetylene with 55 mol% of nitrogen or 70% air prevented spontaneous explosion. At higher dilutions, sparking did not initiate explosion [4]. Explosive interaction of chlorine and acetylene in the dark is initiated by presence of oxygen at between 0.1 and about 40 vol%. The reaction is inhibited by inert gases or oxygen at higher concentrations [5]. Safe techniques for demonstrating explosive combination of acetylene and chlorine have been described [6,7], the latter involving dropping a small lump of calcium carbide into acidified sodium hypochlorite solution. Tetrachloroethane is manufactured by reacting excess chlorine with acetylene at 100°C in presence of ferric chloride. On one occasion the temperature fell to 60°C (low chlorine flow?)and there was an explosion. It was suggested that monochloroacetylene had formed and decomposed, initiating an acetylene/chlorine or gas/air explosion. A number of such explosions have occurred, particularly during start-up [8]. Another explosion was attributed to damp ferric chloride [9].

Heavy metals and salts

See METAL ACETYLIDES

Liquid nitrogen

Houseman, T. H. *et al., J. Labelled Compd. Radiopharm.*, 1978, **14**, 164

Liquid nitrogen should not be used as a trap coolant with acetylene, owing to the explosive nature of liquid or solid acetylene (title reference 5 above).

Mercury(II) salts, Nitric acid, (Sulfuric acid)

See Nitric acid: Acetylene, Mercury(II) salts

Nitric acid, Perchloric acid

See Perchloric acid: Acetylene, Nitric acid

Other reactants

Yoshida, 1980, 15

MRH values calculated for 10 combinations with materials catalysing the decomposition of acetylene are given.

Oxidants

Since acetylene is endothermic (values above) and effectively a reducing agent, its reactions with oxidants are usually violent or explosive if uncontrolled.

See Dinitrogen oxide or Halogens, both above; Oxygen, below
Calcium hypochlorite: Acetylene
Nitric acid: Acetylene, Mercury(II) salts
Nitrogen oxide: Dienes, Oxygen
Ozone: Acetylene
Trifluoromethyl hypofluorite: Hydrocarbons

Oxides of nitrogen

See Nitrogen oxide: Dienes, Oxygen

Oxygen

1. Fowles, G. *et al., School Sci. Rev.*, 1940, **22**(85), 6; 1962, **44**(152), 161; 1963, **44**(154), 706; 1964, **45**(156), 459
2. Kiyama, R. *et al., Rev. Phys. Chem. Japan*, 1953, **23**, 43—48
3. Moye, A., *Chem. Ztg.*, 1922, **46**, 69
4. Ivanov, U., *Chem. Abs.*, 1976, **84**, 57968

The explosion of acetylene—oxygen mixtures in open vessels is a very dangerous experiment (stoicheiometric mixtures detonate with great violence, completely shattering the container). Full precautions are essential for safety [1]. When a mixture of acetylene and oxygen (54:46) at 270°C/10.9 bar was compressed in 0.7 s to 56.1 bar, the resulting explosion attained a pressure of several kbar. In other tests rapid compression of acetylene or its mixtures with air caused no explosions [2]. Previously, passage of acetylene into liquid air to deliberately generate a paste of solid acetylene and liquid oxygen, ‘by far the most powerful of explosives’, had been proposed [3]. Acetylene had been collected for teaching purposes over water in a pneumatic trough. Later, oxygen was collected in the same way without changing the water, and the sample exploded violently when exposed to a glowing splint. Acetylene remaining dissolved in the water had apparently been displaced by the oxygen stream, the lower explosive limit for acetylene being only 2.5% in air, and less in oxygen [4].

Potassium MRH 8.70/tr.

Berthelot, M., *Bull. Soc. Chim. Fr. [2]*, 1866, **5**, 188

Molten potassium ignites in acetylene, then explodes.

Potassium hydroxide

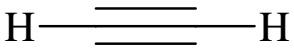
Schildberg, H. P. *et al., Loss Prevention and Safety Promotion in the Process Industries*, (Mewis, Pasman and De Rademaker, eds.), Vol. 1, 401, Amsterdam, Elsevier, 1995

At temperatures above 100° C and pressures above 2 bar, potassium hydroxide powder can initiate self-propagating decomposition of acetylene. More detail on limits is given.

See other ALKYNES

0683. Poly(acetylene)

[25067-58-7] **$(C_2H_2)_n$**



Feast, W. J. *et al., J. Chem. Soc., Chem. Comm.*, 1985, 202—203

The second stage of an improved synthesis of poly(acetylene), which involves disproportionation of a soluble polymer by heating a thin film at 75°C to give 1,2-bis(trifluoromethyl)benzene and poly(acetylene), must not be done in bulk because the reaction then becomes explosive. The earlier synthesis by direct polymerisation of acetylene was considerably more dangerous

See Poly([7,8-bis(trifluoromethyl)tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane-3,4-diyl]-1,2-ethenediyl)

Iodine

See Iodine: Poly(acetylene)

See related DIENES

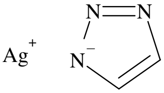
Perchlorate-doping

See PERCHLORATE-DOPED CONDUCTING POLYMERS

See related DIENES

0684. Silver 1,2,3-triazolide

[ ] **$C_2H_2AgN_3$**

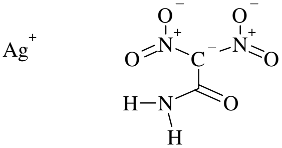


See 1,2,3-Triazole

See other *N*-METAL DERIVATIVES, SILVER COMPOUNDS, TRIAZOLES

0685. Silver dinitroacetamide

[26163-27-9] (ion) **$C_2H_2AgN_3O_5$**



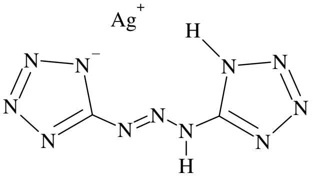
Parker, C. O. *et al., Tetrahedron*, 1962, **17**, 108

The sodium salt explodes at 160°C and the potassium and silver salts at 159 and 130°C, respectively.

See other POLYNITROALKYL COMPOUNDS, SILVER COMPOUNDS

0686. Silver 1,3-di(5-tetrazolyl)triazenide

[ ] **$C_2H_2AgN_{11}$**

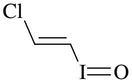


See 1,3-Di(5-tetrazolyl)triazene

See other SILVER COMPOUNDS, TETRAZOLES, TRIAZENES

0687. 2-Iodosovinyl chloride

[ ] **C_2H_2ClIO**



Alone, or Water

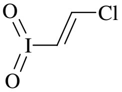
Thiele, J. *et al., Ann.*, 1909, **369**, 131

It explodes at 63°C and contact with water disproportionates it to the more explosive iodyl compound (next below).

See other IODINE COMPOUNDS

0688. 2-Iodylvinyl chloride

[ ] **$C_2H_2ClIO_2$**



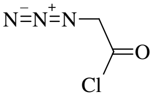
Thiele, J. *et al., Ann.*, 1909, **369**, 131

Explodes violently on impact, friction or heating to 135°C.

See other IODINE COMPOUNDS

0689. Azidoacetyl chloride

[30426-58-5] **$C_2H_2ClN_3O$**



1. Wieland, T. *et al., Chem. Ber.*, 1960, **93**, 1236
2. Prodan, K. A. *et al., Chem. Eng. News*, 1981, **59**(14), 59
3. Hoppe, D. *et al., Ann.*, 1980, 1519

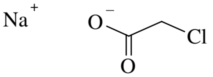
Using a published procedure [1] for preparing azidoacetyl chloride, but at 1.7-fold higher concentration, azidoacetic acid and sulfinyl chloride were slowly heated up to reflux. After 40 min. decomposition started and accelerated to a violent explosion [2]. The cause seems likely to have been the higher initial concentration of azido acid, which would have produced a higher concentration (87%) of acid chloride in excess sulfinyl chloride, and at a significantly higher reflux temperature, than the original method (about 50%). A relatively safe way of preparing the explosively unstable material involves a low temperature partial distillation procedure, but full precautions are recommended [3].

See Azidoacetic acid

See other ORGANIC AZIDES

0690. Sodium chloroacetate

[3926-62-3] **$C_2H_2ClNaO_2$**

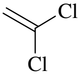


Energy of decomposition (in range 130—220°C) was measured as 0.29kJ/g by DSC, and T_{ait24} was determined as 96°C by adiabatic Dewar tests, with an apparent energy of activation of 112kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

†0691. 1,1-Dichloroethylene (Vinylidene chloride)

[75-35-4] **$C_2H_2Cl_2$**



HCS 1980, 378

1. Reinhardt, R. C., *Chem. Eng. News*, 1947, **25**, 2136
2. *MCA Case History No. 1172*
3. *MCA Case History No. 1693*
4. Harmon, 1974, iv, 2.21
5. Warren, H. S. *et al., Chem. Abs.*, 1978, **89**, 219959

When stored at between —40° and +25°C in the absence of inhibitor and in presence of air, vinylidene chloride rapidly absorbs oxygen with formation of a violently explosive peroxide. The latter initiates polymerisation, producing an insoluble polymer which adsorbs the peroxide. Separation of this polymer in the dry state must be avoided, since if more than 15% of peroxide is present, the polymer may be detonable by slight shock or heat. Hindered phenols are suitable inhibitors to prevent peroxidation [1]. The earlier Case History describes an explosion during handling of a pipe used to transfer the chloride [2]. Two further cases of formation of the polymeric peroxide in bottles of vinylidene chloride in refrigerated storage, and subsequent explosions during handling or disposal, are recorded [3]. The monomer is normally handled at —10°C in absence of light or water, which tend to promote self-polymerisation [4]. Hazards from explosions when the chloride is stored or handled in presence of air are discussed [5].

See entry POLYMERISATION INCIDENTS, POLYPEROXIDES, VIOLENT POLYMERISATION

Chlorotrifluoroethylene

Raasch, M. S. *et al., Org. Synth.*, 1962, **42**, 46

Condensation of the reactants at 180°C under pressure to give 1,1,2-trichloro-2,3,3-trifluorocyclobutane was effected smoothly several times in a 1 l autoclave. Scaling up to a 3 l preparation led to uncontrollable polymerisation which distorted the larger autoclave.

Ozone

'Vinylidene Chloride Monomer', 9, Midland (Mich.), Dow Chemical Co., 1968

The reaction products formed with ozone are particularly dangerous.

See other OZONIDES

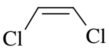
Perchloryl fluoride

See Perchloryl fluoride: Hydrocarbons, etc.

See other HALOALKENES, PEROXIDISABLE COMPOUNDS

†0692. *cis*-1,2-Dichloroethylene

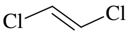
[156-60-5] **$C_2H_2Cl_2$**



See other HALOALKENES

†0693. *trans*-1,2-Dichloroethylene

[156-59-2] **$C_2H_2Cl_2$**



1. Anon., *BCISC Quart. Safety Summ.*, 1964, **35**, 37
2. Anon., *Sichere Chemiearb.*, 1964, **16**, 35

Under appropriate conditions, dichloroethylene, previously thought to be non-flammable, can cause a fire hazard [1]. Addition of a hot liquid to the cold solvent caused sudden emission of sufficient vapour to cause a flame to flash back 12 m from a fire. Although the bulk of the solvent did not ignite, various items of paper and wood in the room were ignited by the transient flame [2].

Alkalies

1. Anon., *Fire Accid. Prev.*, 1956, **42**, 28
2. Thron, H., *Chem. Ztg.*, 1924, **48**, 142

1,2-Dichloroethylene in contact with solid caustic alkalies or their conc. solutions will form chloroacetylene which ignites in air [1]. Distillation of ethanol containing

0.25% of the halocarbon with aqueous sodium hydroxide gave a product which ignited in air [2].

1,1,2,2-Tetrachloroethane: Alkalies

See Trichloroethylene: Alkali

Difluoromethylene dihypofluorite

See Difluoromethylene dihypofluorite: Haloalkenes

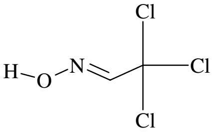
Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Halocarbons

See other HALOALKENES

0694. Trichloroacetaldehyde oxime

[1117-99-3] **$C_2H_2Cl_3NO$**



Alkali

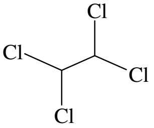
Rodd, 1965, Vol. 1C, 46

The oxime decomposes explosively with alkali, forming hydrogen cyanide, hydrogen chloride and carbon dioxide.

See other GAS EVOLUTION INCIDENTS, OXIMES

0695. 1,1,2,2-Tetrachloroethane

[79-34-5] **$C_2H_2Cl_4$**



(*MCA SD-34*, 1949); *HCS 1980*, 886

Alkalis

MCA SD-34, 1949

It is not an inert solvent, and on heating with solid potassium hydroxide or other base, hydrogen chloride is eliminated and chloro- or dichloro-acetylene, which ignite in air, are formed.

Metals

Sodium: Halocarbons

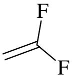
See Potassium: Halocarbons

See METAL—HALOCARBON INCIDENTS

See other HALOALKANES

†0696. 1,1-Difluoroethylene (Vinylidene fluoride)

[75-38-7] **$C_2H_2F_2$**



HCS 1980, 409

Hydrogen chloride

Jensen, J. H., *Chem. Eng. News*, 1981, **59**(14), 3, 59

As well as the normal addition reaction, an extremely exothermic decomposition reaction may occur, particularly at high vessel loadings. At loadings of 0.8 ml of 1:1 mixture per ml, the violent reaction, catalysed by iron(III) chloride, initiates at —40°C and will attain pressures above 0.7 kbar at the rate of 14 kbar/s. At 0.5 ml loading density, a maximum pressure of 68 bar, attained at 114 bar/s, was observed.

See entry CATALYTIC IMPURITY INCIDENTS, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

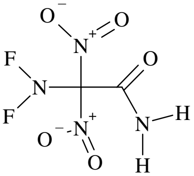
Ozone

See Ozone: 1,1-Difluoroethylene

See other HALOALKENES

0697. 2-(Difluoroamino)-2,2-dinitroacetamide

[180570-38-1] **$C_2H_2F_2N_4O_5$**

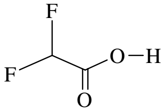


See 1,1-DINITRODIFLUORAMINES

See other N-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

0698. Difluoroacetic acid

[381-73-7] **$C_2H_2F_2O_2$**



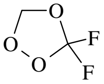
Caesium fluoride, Fluorine

See Fluorine: Caesium fluoride, etc.

See other ORGANIC ACIDS

0699. 1,1-Difluoroethylene ozonide (3,3-Difluoro-1,2,4-trioxolane)

[69932-17-8] **$C_2H_2F_2O_3$**

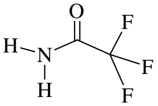


See Ozone: 1,1-Difluoroethylene

See other OZONIDES

0700. Trifluoroacetamide

[354-38-1] **$C_2H_2F_3NO$**

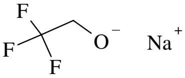


Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Fluoroamides

0701. Sodium 2,2,2-trifluoroethoxide

[420-87-1] **$C_2H_2F_3NaO$**



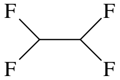
Schmutz, J. L. *et al., Inorg. Chem.*, 1975, **14**, 2437

During preparation from sodium and excess alcohol in ether, attempts to remove last traces of the alcohol by warming under vacuum led to explosions.

See related METAL ALKOXIDES

0702. 1,1,2,2-Tetrafluoroethane

[811-97-2] **$C_2H_2F_4$**



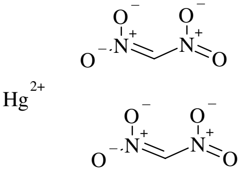
Schröder, V. *et al. Loss Prevention and Safety Promotion in the Process Industries* Vol II (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 339, Amsterdam, Elsevier, 1995

Although not flammable under normal conditions in air, it is at elevated pressure, or with oxygen enrichment. Explosive limits are reported and reviewed.

See also FLUOROCARBONS

0703. Mercury(II) *aci*-dinitromethanide

[ ] **$C_2H_2HgN_4O_8$**



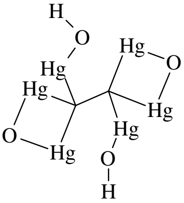
Urbanski, 1967, Vol. 3, 158

This salt of *aci*-dinitromethane shows detonator properties.

See other aci-NITRO SALTS, MERCURY COMPOUNDS

0704. 1,2-Bis(hydroxomercurio)-1,1,2,2-bis(oxydimercurio)ethane (‘Ethane hexamercarbide’)

[67536-44-1] **$C_2H_2Hg_6O_4$**



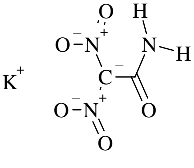
Hofmann, K. A., *Ber.*, 1898, **31**, 1904

The compound, formulated as above, explodes very violently at 230°C.

See other MERCURY COMPOUNDS

0705. Potassium dinitroacetamide

[50650-92-5] **$C_2H_2KN_3O_5$**

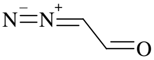


See Silver dinitroacetamide

See other POLYNITROALKYL COMPOUNDS

0706. Diazoacetaldehyde

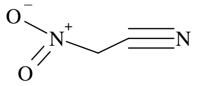
[6832-13-9] **$C_2H_2N_2O$**



Arnold, Z., *Chem. Comm.*, 1967, 299

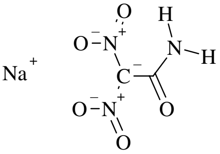
It may be distilled out continuously as formed at 40°C/13 mbar, but readily detonates with great violence if overheated.
See other ALDEHYDES, DIAZO COMPOUNDS

0707. 2-Nitroethanonitrile (Nitroacetonitrile) (Nitromethyl cyanide)
[ ] **$CH_2N_2O_2$**



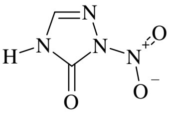
Koenig, L. *et al.*, Personal communication, 1997
Made by dehydration of nitroacetaldehyde oxime, this is an explosion hazard. It is improbable that the nitrile is not, itself, detonable.
See 2-Nitroacetaldehyde oxime
See other C—NITRO COMPOUNDS

0708a. Sodium dinitroacetamide
[26163-27-9] (ion) **$C_2H_2N_3NaO_5$**



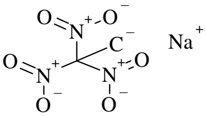
See Silver dinitroacetamide
See other POLYNITROALKYL COMPOUNDS

0708b. 1-Nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one
[ ] **$C_2H_2N_4O_3$**



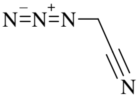
Zbarskii, V. L. *et al., Russian J, Org, Chem.*, 2004, **40**(7) 1069
The compound is described as a nitrating agent. It is also described as an explosive.
See other *N*—NITRO COMPOUNDS

0709. Sodium 2,2,2-trinitroethanide
[ ] **$C_2H_2N_3O_6Na$**



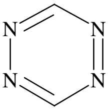
See *N,N′*-Bis(trinitroethyl)urea
See other POLYNITROALKYL COMPOUNDS

0710. Azidoacetonitrile
[57707-64-9] **$C_2H_2N_4$**



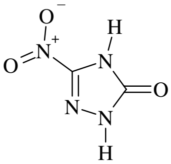
Freudenberg, K. *et al., Ber.*, 1932, **65**, 1188
With over 51% nitrogen content, it is, as expected, explosive, sensitive to impact or heating to 250°C.
See other CYANO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

0711. 1,2,4,5-Tetrazine
[290-96-0] **$C_2H_2N_4$**



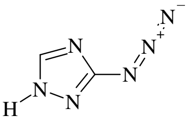
Sulfuric acid
Sorbe, 1968, 139
The solid base decomposes violently in contact with conc. acid.
See other HIGH-NITROGEN COMPOUNDS, ORGANIC BASES

0712. 3-Nitro-1,2,4-triazolone (Oxynitrotriazole)
[932-64-9] **$C_2H_2N_4O_3$**



Ullmann, 1987, A10, 162
Finds employment as an high explosive (oxygen balance —40%).
See EXPLOSIVES, OXYGEN BALANCE
See other HIGH-NITROGEN COMPOUNDS, NITRO COMPOUNDS, TRIAZOLES

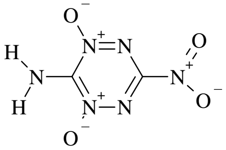
0713. 3-Azido-1,2,4-triazole
[21041-85-0] **$C_2H_2N_6$**



Denault, G. C. *et al., J. Chem. Eng. Data*, 1968, **13**, 514
Samples exploded during analytical combustion.
See other ORGANIC AZIDES, TRIAZOLES

0714. 3-Amino-6-nitro-1,2,4,5-tetrazine-2,4-dioxide

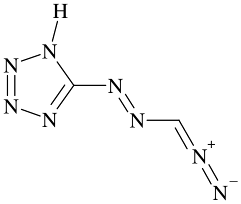
[153757-95-0] **$C_2H_2N_6O_4$**



See 3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide
See also AMINE OXIDES
See other HIGH-NITROGEN COMPOUNDS

0715. 5-(Diazomethylazo)tetrazole

[ ] **$C_2H_2N_8$**

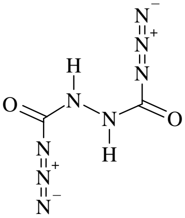


Mayants, A. G. *et al., Zh. Org. Khim.*, 1991, **27**(11), 2450; *Chem. Abs.*, 1992, **116**, 234937

The compound, produced as an hydrate from dilute acid hydrolyses of disodium azotetrazolide, exploded on heating for analytical purposes.
See other AZO COMPOUNDS, DIAZO COMPOUNDS, TETRAZOLES

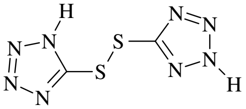
0716. 1,2-Diazidocarbonylhydrazine

[67880-17-5] **$C_2H_2N_8O_2$**



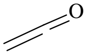
Kesting, W., *Ber.*, 1924, **57**, 1321
Similar in properties to lead or silver azide, it explodes on heating or impact.
See other ACYL AZIDES, HIGH-NITROGEN COMPOUNDS

0717. 5,5′-Tetrazolyl disulfide (5,5′-Dithiobis[1*H*]tetrazole)
[72848-18-1] **$C_2H_2N_8S_2$**



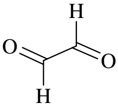
Christensen, T. B. *et al., Sulfur Lett.*, 1993, **16**(5-6), 205
In a paper devoted to tetrazole chemistry, the explosive nature of this compound excited comment.
See also HIGH-NITROGEN COMPOUNDS
See other TETRAZOLES

0718. Ketene (Ethenone)
[463-51-4] **C_2H_2O**



Hydrogen peroxide
See Hydrogen peroxide: Ketene

†0719. Ethanedial (Glyoxal)
[107-22-2] **$C_2H_2O_2$**



HCS 1980, 522

Alone, or Water
1. Merck, 1983, 647
2. van den Brink, M. J., *Chemisch Magazine* (Rijswijk), 1982, (7—8), 428

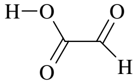
A powerfully reducing and reactive solid (m.p., 15°C) of high vapour pressure (b.p., 50°C). Mixtures with air may explode, and contact with water causes violent polymerisation [1]. More usually encountered polymeric or as a hydrate. Like formaldehyde, pure glyoxal may polymerise exothermally and ignite in storage [2].

Nitric acid, Water
See Nitric acid: Glyoxal
See other ALDEHYDES, REDUCANTS

Preparative hazard
See Nitric acid: 2,4,6-Trimethyltrioxane

0720. Glyoxylic acid (Oxoacetic acid)

[298-12-4] **$C_2H_2O_3$**



Preparative hazard

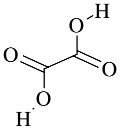
See Nitric acid: Glyoxal

See other ORGANIC ACIDS

See related ALDEHYDES

0721. Oxalic acid (Ethanedioic acid)

[144-62-7] **$C_2H_2O_4$**



NSC 406, 1978; *HCS 1980*, 706

CHETAH, 1990, 184

Surprisingly, even the dihydrate is apparently detonated by a 50g tetryl booster, the anhydrous acid is thermally less stable and thus probably more sensitive. There is, however, no history of explosion.

Other reactants

Yoshida, 1980, 178

MRH values calculated for 5 combinations are given.

Silver

See Silver: Carboxylic acids

Sodium chlorite

See Sodium chlorite: Oxalic acid

Urea

von Bentzinger, R. *et al., Praxis Naturwiss. Chem.*, 1987, **36**(8), 41—42

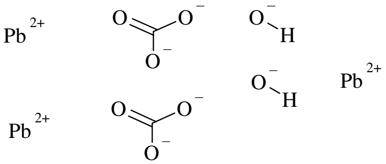
During the qualitative analysis of an ‘unknown’ mixture of oxalic acid, urea and a little charcoal, a sample was put in an ignition tube under a layer of granular copper oxide, topped by glass wool and a little anhydrous copper sulfate (to detect evolved water). The top end of the tube was drawn down obliquely into a capillary so that the pyrolysis gases could be passed into barium hydroxide solution (to detect carbon dioxide). It was not noticed that the end of the capillary was sealed, and when the sample was heated in a flame, an unexpectedly violent explosion followed. Later experiments showed that there was no explosion if oxalic acid alone, or urea alone, was heated with copper oxide in a sealed tube, but that a mixture of the two always led to a violent explosion. The same also happened in absence of copper oxide. Further work (DSC, and measurement of volumes of gas liberated) led to the conclusions that the reactions involved were:

$$2CO.(NH_2)_2 + 3(CO.OH)_2 \rightarrow 5CO_2 + 3CO + 4NH_3 + H_2O$$

and that a gas pressure approaching 100 bar would be produced in the accidentally sealed ignition tube at 570°C.

See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS, ORGANIC ACIDS, REDOX REACTIONS

0722. Lead carbonate—lead hydroxide (Basic lead carbonate)
[598-63-0] **$C_2H_2O_8Pb_3$**

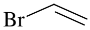


Fluorine

See Fluorine: Metal salts

See other INORGANIC BASES

†0723. Bromoethylene (Vinyl bromide)
[593-60-2] **C_2H_3Br**

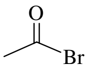


1. *HCS 1980*, 956
2. *DOC 5*, 1982, 799

The highly flammable gas reacts violently with oxidants [1] and may polymerise in sunlight [2].

See other HALOALKENES

0724. Acetyl bromide
[506-96-7] **C_2H_3BrO**



HCS 1980, 108

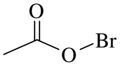
Hydroxylic compounds

Merck, 1976, 11

Interaction with water, methanol or ethanol is violent, hydrogen bromide being evolved.

See other ACYL HALIDES

0725. Acetyl hypobromite
[4254-22-2] **$C_2H_3BrO_2$**

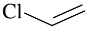


1. Reilly, J. J. *et al., J. Org. Chem.*, 1974, **39**, 3992
2. Skell, P. S. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 4000, 4007

The instability of the hypobromite is noted, and protective shielding is recommended for work with more than 5 g quantities [1]. Though stable in fluorotrichloromethane solution at —23°C under nitrogen in the dark, the isolated solid exploded at —23°C at below 1.2 mbar [2].

See other ACYL HYPOHALITES

†0726. Chloroethylene (Vinyl chloride)
[75-01-4] **C_2H_3Cl**



(*MCA SD-56*, 1972); *HCS 1980*, 957; *RSC Lab. Hazards Data Sheet No. 56*, 1987

1. *MCA Case History No. 625*
2. Harmon, 1974, 2.20, 4.74—4.77
3. *MCA Case History No. 1551*
4. Scali, C. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 1350—1358, Basle, SSCI, 1980
5. Anon., *Eur. Chem. News*, 1993, **60**(1589), 26

Discharge of a spray of vapour and liquid under pressure from a cylinder into a fume hood generated static and ignited the vapour. Discharge of the vapour phase only did not lead to ignition [1]. Vinyl chloride tends to self-polymerise explosively if peroxidation occurs, and several industrial explosions have been recorded [2]. Accidental exposure of the recovered monomer to atmospheric oxygen for a long period caused formation of an unstable polyperoxide which initiated an explosion. Suitable precautions are discussed, including the use of 20—30% aqueous sodium hydroxide solution to destroy the peroxide [3]. Problems of stability and control of batch reactors for the suspension polymerisation of vinyl chloride have been studied in relation to process kinetics and plant heat transfer coefficients [4]. A polymerisation reaction ran beyond control, generating back pressure which caused the monomer to leak through a valve, forming a vapour cloud which ignited and exploded [5].

See 1,1-Dichloroethylene

See VIOLENT POLYMERISATION

See other POLYMERISATION INCIDENTS, POLYPEROXIDES, STATIC INITIATION INCIDENTS, VAPOUR CLOUD EXPLOSIONS

Oxides of nitrogen

Povey, R., private comm., 1979

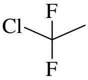
An explosion in a valve in a liquid monomer line was ascribed to traces of oxides of nitrogen remaining after the valve had been passivated by treatment with nitric acid.

Oxygen

Tartari, V., *Proc. 34th Ital. Chem. Congr. Safety Chem. Proc.*, 51—60, Milan, 1983
The stability of the monomer to heat in the presence (and absence) of oxygen has been studied by ARC. The intensity of the exotherm at 90—100°C depends on the partial pressure of oxygen.
See other HALOALKENES, PEROXIDISABLE COMPOUNDS

†0727. 1-Chloro-1,1-difluoroethane

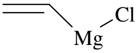
[75-68-3] **$C_2H_3ClF_2$**



Difficult to ignite vapour
See FLASH POINTS (reference 19)
See other HALOALKANES

0728. Ethenylmagnesium chloride (Vinylmagnesium chloride) (Chloroethenylmagnesium)

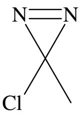
[3536-96-7] **C_2H_3ClMg**



Rittmeyer, P. *et al., Z. Naturforsch., B: Chem. Sci.*, 1993, **48**(9), 1223
An incident during concentration of a tetrahydrofuran solution on pilot plant led to a study of the concentration dependent exothermic decomposition of the reagent and generation of safety rules.
See other GRIGNARD REAGENTS

0729. 3-Chloro-3-methyldiazirine

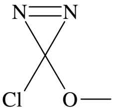
[4222-21-3] **$C_2H_3ClN_2$**



1. Liu, M. T. H., *Chem. Eng. News*, 1974, **53**(36), 10
2. Jones, W. E. *et al., J. Photochem.*, 1976, **5**, 233—239
3. Frey, H. M. *et al., J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 2011

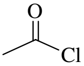
Extremely shock-sensitive and violently explosive; initiation has been caused by prolonged freezing at —196°C, or by sawing a stopcock off a metal trap containing trace amounts [1]. It may be stored safely at —80°C [2]. Detonative explosion during trap-to-trap distillation of purified material is noted [3].
See other DIAZIRINES

0730. 3-Chloro-3-methoxydiazirine
[4222-27-9] **$C_2H_3ClN_2O$**



Smith, N. P. *et al., J. Chem. Soc., Perkin Trans. 2*, 1979, 213
Unpredictably explosive as the neat liquid, it may be handled safely in solution. All distillation traps must contain solvent.
See other DIAZIRINES

†0731. Acetyl chloride (Ethanoyl chloride)
[75-36-5] **C_2H_3ClO**



FPA H65, 1978; *HCS 1980*, 109

Dimethyl sulfoxide
See Dimethyl sulfoxide: Acyl halides

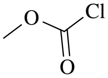
Other reactants
Yoshida, 1980, 51
MRH values calculated for 13 combinations with oxidants are given.

Preparative hazard
See Phosphorus trichloride: Carboxylic acids

Water
1. *Haz. Chem. Data*, 1975, 30
2. Anon., *CISHC Chem. Safety Summ.*, 1986, **57**(225), 3
3. Anon., personal communication 1997

Interaction is violent [1]. A polythene-lined drum which had previously contained acetyl chloride was inspected and appeared empty, but when it was washed out with water a violent eruption occurred. This was attributed to trapping of residual acetyl chloride between the split liner and the drum wall [2]. A very similar but more violent event, rupturing the drum and sending part of it 30 m. with sufficient force to puncture another drum which it hit, occurred in Scotland in 1997 [3].
See other ACYL HALIDES

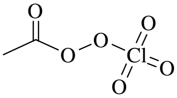
†0732. Methyl chloroformate (Methyl carbonochloridate)
[79-22-1] **$C_2H_3ClO_2$**



HCS 1980, 645

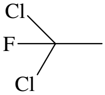
See other ACYL HALIDES

0733. Peroxyacetyl perchlorate
[66955-43-9] **$C_2H_3ClO_6$**



Yakovleva, A. A. *et al., Chem. Abs.*, 1979, **91**, 210847
The peroxyester of +9.1% oxygen balance exploded on detonation or friction.
See Peroxypropionyl perchlorate
See related ALKYL PERCHLORATES, PEROXYESTERS

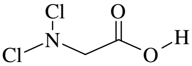
0734. 1,1-Dichloro-1-fluoroethane
[1717-00-6] **$C_2H_3Cl_2F$**



1. Anon., *Sichere Chemiearbeit*, 1993, **45**(8), 105
2. Bretherick, L., *Chem. Eng. News*, 1988, **66**(50), 2

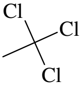
An ‘empty’ drum which had contained this exploded when cut into by a grinder. It is presumably more flammable than might be anticipated [1]. Like trichloroethane the vapour is difficult to ignite and may not show a flash point, but can form explosive mixtures with air [2].
See other HALOALKANES

0735. *N,N*-Dichloroglycine
[58941-14-3] **$C_2H_3Cl_2NO_2$**



Vit, J. *et al., Synth. Comm.*, 1976, **6**(1), 1—4
It explodes at 65°C, so solutions must be evaporated at below 40°C.
See other *N*-HALOGEN COMPOUNDS, ORGANIC ACIDS

†0737. 1,1,1-Trichloroethane
[71-55-6] $C_2H_3Cl_3$



(*MCA SD-90*, 1965); *HCS 1980*, 918; *RSC Lab. Hazard Data Sheet No. 1*, 1982

1. Wrightson, I. *et al., Loss Prev. Bull.*, 1988, (083), 21—23
2. Santon, R. C. *et al., Proc. 6th Int. Sympos. Loss Prev. Safety Prom. Process Ind.*, 1989, Oslo, Norweg. Soc. Chem. Eng., in press

Although no flash point is measurable by standard tests, the vapour can be ignited by a high-energy source, the limits being 8.0—10.5 vol% in air at 25°C, with an auto-ignition temperature of 500°C. A 1050 m^3 storage tank containing 70 t of the inhibited solvent, normally blanketted with nitrogen to exclude moisture, had developed gas leaks in the roof, and the purge system had been switched to manual control. Previous withdrawal of 1150 t had drawn in air, which had not been effectively displaced by manual purging. Arc-welding to repair the roof leaks led to an explosion which separated the roof from the tank for 65% of the 36 m circumference. Only one other explosion, when the end of an 'empty' 200 l drum was cut with an oxy-acetylene torch, has been reported [1]. New work has extended downwards the temperature limits for ignition to 10°C for lel of 8.0 vol%, and 22° for uel of 14.2 vol%. These values diverge with increasing temperature to 6% and 15.5%, respectively, at 100°C [2].

See FLASH POINTS (reference 19)

Aluminium oxide, Heavy metals
See Aluminium oxide: Halocarbons, etc.

Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Halocarbons

Inhibitors
See FLASH POINTS (reference 19)

Metals
See Aluminium: Halocarbons
Magnesium: Halocarbons
METAL—HALOCARBON INCIDENTS
Potassium: Halocarbons
Potassium—sodium alloy: Halocarbons

Molecular sieve
1. Salmon, J. *et al., Chem. & Ind.*, 1995, 814
2. Wilson, W., *Chem. & Ind.*, 1995, 854
3. Bretherick, L., personal communication
4. Winterton, N. *et al., Chem. & Ind.*, 1995, 902
5. Whitmore M. W. *et al., Chem. & Ind.*, 1995, 942

Some unstabilised trichloroethane had stood over molecular sieve (uncertain which grade) for a period of some years. The sieve was filtered out and the bottle, still containing some sieve, purged with nitrogen, after which it exploded when moved. The remaining sieve deflagrated on addition to a bucket of water [1]. It is suggested that the sieve catalysed dehydrochlorination to chloroacetylene, which is explosive [2]. This seems improbable since the acetylene is also volatile and not very polar, thus should not adhere to the dried sieve. An alternative explanation is that dehydrochlorination occured, giving vinylidene chloride (1,1-dichloroethene) which polymerised with atmospheric oxygen as a comonomer, leading to a polyperoxide which would adhere to the sieve [3,4]. Another sample of ancient trichloroethane, stored over sieves, showed no instability or peroxidation [5].

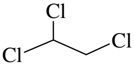
Oxygen

See Oxygen (Gas): Halocarbons
Oxygen (Liquid): Halocarbons

See other HALOALKANES

0738. 1,1,2-Trichloroethane

[79-00-5] **$C_2H_3Cl_3$**



HCS 1980, 917

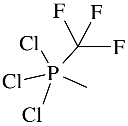
Potassium

See Potassium: Halocarbons

See other HALOALKANES

0739. Methyltrifluoromethyltrichlorophosphorane

[69517-30-2] **$C_2H_3Cl_3F_3P$**

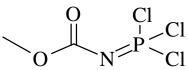


Preparative hazard

See Tetrachlorotrifluoromethylphosphorane: Tetramethyllead

0740. *N*-Carbomethoxyiminophosphoryl chloride

[25147-05-1] **$C_2H_3Cl_3NO_2P$**

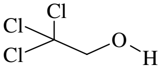


Mellor, 1971, Vol. 8, Suppl. 3, 589

This intermediate (or its ethyl homologue), produced during the preparation of phosphoryl dichloride isocyanate from interaction of phosphorus pentachloride and

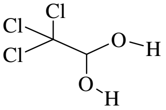
methyl (or ethyl) carbamate, is unstable. Its decomposition to the required product may be violent or explosive unless moderated by presence of a halogenated solvent.
See related NON-METAL HALIDES

0741. 2,2,2-Trichloroethanol
[115-20-8] **$C_2H_3Cl_3O$**



Sodium hydroxide
MCA Case History No. 1574
Accidental contact of 50% sodium hydroxide solution with residual trichloroethanol in a pump caused an explosion. This was confirmed in laboratory experiments. Chlorohydroxyacetylene, or the isomeric chloroketene, or chlorooxirene may have been formed by elimination of hydrogen chloride.
See related HALOALKANES

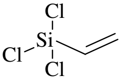
0742. 2,2,2-Trichloro-1,1-ethanediol (Chloral hydrate)
[302-17-0] **$C_2H_3Cl_3O_2$**



1. Marvel, C. S. *et al., Org. Synth.*, 1941, Coll. Vol. 1, 377
2. Goodwin, B., *Chem. Brit.*, 1988, **24**, 336
3. Gandy, R. *et al., Chem. Brit.*, 1988, **24**, 336

Following a published procedure for converting substituted anilines to isatins by reaction with chloral hydrate and hydroxylamine [1], it was noticed that at the end of the first stage (formation of an isonitrosoacetanilide), the odour of hydrogen cyanide was present, and this was confirmed by a Prussian blue test [2]. In related work, concentrations of 100—200 ppm of hydrogren cyanide were found [3]. A mechanism for its formation from chloral hydrate and hydroxylamine was proposed [2], and the need for appropriate precautions was stressed [2,3].
See other GAS EVOLUTION INCIDENTS

†0743. Trichlorovinylsilane (Ethenyltrichlorosilane)
[75-94-5] **$C_2H_3Cl_3Si$**

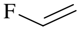


It may ignite in air.

Water
491M, 1975, 426

It reacts violently with water or moist air.
See related ALKYLHALOSILANES

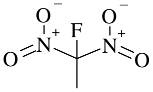
†0744. Fluoroethylene (Vinyl fluoride)
[75-02-5] **C_2H_3F**



HCS 1980, 958

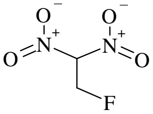
Ozone
See Fluoroethylene ozonide
See other HALOALKENES

0745. 1-Fluoro-1,1-dinitroethane
[13214-58-9] **$C_2H_3FN_2O_4$**



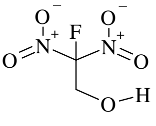
See entry FLUORODINITROMETHYL COMPOUNDS

0746. 2(?)-Fluoro-1,1-dinitroethane
[68795-10-8] **$C_2H_3FN_2O_4$**



MCA Case History No. 784
During a prolonged fractional distillation of the material at 75°C/50 mbar, an exothermic decomposition began. As a remedial measure (!), air was admitted to the hot decomposing residue, causing a violent explosion. Admission of nitrogen and/or cooling the residue before admitting air might have avoided the incident.
See related FLUORODINITROMETHYL COMPOUNDS

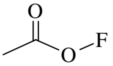
0747. 2-Fluoro-2,2-dinitroethanol
[17003-75-7] **$C_2H_3FN_2O_5$**



1. Cochoy, R. E. *et al., J. Org. Chem.*, 1972, **37**, 3041
2. Cochoy, R. E. *et al., J. Org. Chem.*, 1990, **55**(4), 1401

It is a potentially explosive vesicant, from which a series of esters, expected to be explosive, was prepared [1]. During concentration of a dichloromethane solution, there is a sensitivity maximum between 30% solution and the pure compound [2].
See other FLUORODINITROMETHYL COMPOUNDS, POLYNITROALKYL COMPOUNDS

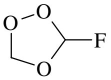
0748. Acetyl hypofluorite
[78948-09-1] **$C_2H_3FO_2$**



1. Adam, M. J., *Chem. & Eng. News*, 1985, **63**(7), 2
2. Appelman, E. *et al., J. Amer. Chem. Soc.*, 1985, **107**, 6516—6518

A minor explosion in the use of gaseous acetyl hypofluorite was caused by inadvertent contact of the gas inlet tube with a cooling bath, which condensed liquid hypofluorite which subsequently exploded on contact with organic material or air [1]. More detail on the isolation of this compound of limited stability, particularly in the liquid phase, is given [2].
See other ACYL HYPOHALITES, OXIDANTS

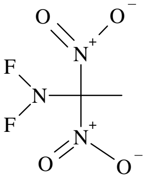
0749. Fluoroethylene ozonide (3-Fluoro-1,2,4-trioxolane)
[60553-18-6] **$C_2H_3FO_3$**



1. Mazur, W. *et al., J. Org. Chem.*, 1979, **44**, 3183
2. Hillig, K. W. *et al., J. Amer. Chem. Soc.*, 1982, **104**, 991

During ozonolysis of vinyl fluoride an explosive solid residue is produced, and the volatile ozonide, trapped at —63°C, may explode spontaneously or during removal by syringe [1]. During the cryogenic distillation of the ozonide (formulated as a trioxolane), several explosions occurred, and the explosive reaction residue was destroyed by digestion with 5% potassium iodide solution for 24 h [2].
See other OZONIDES

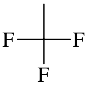
0750. 2-(Difluoroamino)-2,2-dinitroethane
[121832-04-0] **$C_2H_3F_2N_3O_4$**



See 1,1-DINITRODIFLUORAMINES
See other *N*-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

†0751. 1,1,1-Trifluoroethane

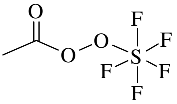
[420-46-2] **$C_2H_3F_3$**



See other HALOALKANES

0752. Pentafluorosulfur peroxyacetate

[60672-60-8] **$C_2H_3F_5O_3S$**



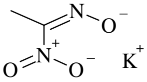
Hopkinson, M. J. *et al., J. Fluorine Chem.*, 1976, **7**, 505

The peroxyester and its homologues, like other fluoroperoxy compounds, are potentially explosive and may detonate on thermal or mechanical shock.

See related FLUORINATED PEROXIDES AND SALTS, PEROXYESTERS

0753. Potassium 1-nitroethane-1-oximate

[3454-11-3] **$C_2H_3KN_2O_3$**



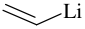
Rodd, 1965, Vol. 1B, 98

Isolated salts of 'nitrolic acids', produced by action of nitrous acid on 1-nitroalkanes, are explosive.

See related NITROALKANES, OXIMES

0754. Vinyllithium

[917-57-7] **C_2H_3Li**



Juenge, E. C. *et al., J. Org. Chem.*, 1961, **26**, 564

When freshly prepared, it is violently pyrophoric but on storage it becomes less reactive and slow to ignite in air, possibly owing to polymerisation.

See related ALKYLMETALS

†0755. Acetonitrile (Ethanenitrile)

[75-05-8] **C_2H_3N**

NSC 683, 1981; *FPA H108*, 1981; *HCS 1980*, 104
RSC Lab. Hazard Data Sheet No. 31, 1984

A moderately endothermic compound (ΔH_f° (l) +53.1 kJ/mol, 1.29 kJ/g) which, though reactive, does not exhibit inherent instability under normal conditions.

Chlorine fluoride, Fluorine
See Fluorine: Acetonitrile, etc.

2-Cyano-2-propyl nitrate
See NITRATING AGENTS

Dinitrogen tetraoxide, Indium
See Dinitrogen tetraoxide: Acetonitrile, Indium

Diphenyl sulfoxide, Trichlorosilane
See Trichlorosilane: Acetonitrile, etc.

N-Fluoro compounds
Fraser, G. W. *et al., Chem. Comm.*, 1966, 532
Nitrogen—fluorine compounds are potentially explosive in contact with acetonitrile.
See Tetrafluorourea: Acetonitrile

Iron(III) perchlorate
See Iron(III) perchlorate: Acetonitrile

Lanthanide perchlorate
Forsberg, J. H., *Chem. Eng. News*, 1984, **62**(6), 33
A solution of an unspecified lanthanide perchlorate in acetonitrile detonated while being heated under reflux.
See other METAL PERCHLORATES, SOLVATED OXOSALT INCIDENTS

Nitric acid MRH 6.15/77
See Nitric acid: Acetonitrile

Nitrogen oxide, base
Sodium methanetris(diazeniumdiolate)

Other reactants
Yoshida, 1980, 19
MRH values calculated for 14 combinations with oxidants are given.

Perchloric acid
See Perchloric acid: Acetonitrile

Sulfuric acid, Sulfur trioxide MRH Sulfuric acid 1.76/54
Lee, S. A., private comm., 1972
A mixture of acetonitrile and sulfuric acid on heating (or self-heating) to 53°C underwent an uncontrollable exotherm to 160°C in a few seconds. The presence of 28 mol% of sulfur trioxide reduces the initiation temperature to about 15°C. Polymerisation of the nitrile is suspected.
See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

0756. Methyl isocyanide

[593-75-9] **C_2H_3N**

$$-\overset{+}{N}\equiv C^{-}$$

1. Lemoult, M. D., *Compt. rend.*, 1906, **143**, 902
2. Stein, A. R., *Chem. Eng. News*, 1968, **46**(45), 7—8
3. Collister, J. L., *Diss. Abs. Intl. B*, 1977, **37**, 4479
4. Pritchard, H. O., *Can. J. Chem.*, 1979, **57**, 2677—2679

It is very endothermic (ΔH_f° (g) $+150.2$ kJ/mol, 3.66 kJ/g). A sample exploded when heated in a sealed ampoule [1], and during redistillation at 59°C/1 bar, a drop of liquid fell back into the dry boiler flask and exploded violently [2]. The explosive decomposition has been studied in detail [3], and existing data on thermal explosion parameters have been re-examined and discrepancies eliminated [4].

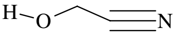
See Ethyl isocyanide

See other ENDOTHERMIC COMPOUNDS

See related CYANO COMPOUNDS

0757. Glycolonitrile (Hydroxyacetonitrile)

[107-16-4] **C_2H_3NO**



1. Anon., *BCISC Quart. Safety Summ.*, 1964, **35**, 2
2. Gaudry, R., *Org. Synth.*, 1955, Coll. Vol. 3, 436
3. Anon., *Chem. Eng. News*, 1966, **44**(49), 50
4. Parker, A. J. *et al., Aust. J. Chem.*, 1978, **31**, 1187

A year-old bottled sample, containing syrupy phosphoric acid as stabiliser and which already showed signs of tar formation, exploded in storage. The pressure explosion appeared to be due to polymerisation, after occlusion of inhibitor in the tar, in a container in which the stopper had become cemented by polymer [1]. A similar pressure explosion occurred when dry redistilled nitrile, stabilised with ethanol [2], polymerised after 13 days [3]. The spontaneous and violent decomposition of the nitrile on standing for more than a week is usually preceded by formation of a red polymer [4].

See other POLYMERISATION INCIDENTS

Alkali

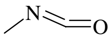
Sorbe, 1968, 146

Traces of alkali promote violent polymerisation.

See other CYANO COMPOUNDS

†0758. Methyl isocyanate

[624-83-9] **C_2H_3NO**



HCS 1980, 570

1. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 93
2. Author's comments
3. Anon., *Chem. & Ind.*, 1985, 202
4. Anon., *Loss Prev. Bull.*, 1985, (063), 1—8
5. Worthy, W., *Chem. Eng. News*, 1985, **63**(6), 27—33
6. D'Silva, T. D. J., *J. Org. Chem.*, 1986, **51**, 3781—3788
7. Bowander, B. *et al., J. Haz. Mat.*, 1988, **19**, 237—269

Bottled samples had been supplied 3 years previously packed in vermiculite in sealed cans. The caps had disintegrated in storage allowing the volatile contents to escape into the external can. When this was pierced, a jet of isocyanate sprayed out uncontrollably. Improved caps are now used for this material [1].

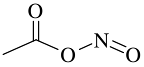
There was a disastrous release of methyl isocyanate at Bhopal in December 1984 which caused over 2000 fatalities. Although making it in a continuous process, the plant stored several weeks supply of the isocyanate. An exothermic reaction in one of the buried 13 m^3 methyl isocyanate storage vessels raised the internal temperature to above the boiling point (39°C). A cooling system existed but appears to have been turned off at the time. The continuing exotherm caused a further substantial increase in pressure, which was eventually relieved through the emergency alkali scrubber and flare stack system. Unfortunately the scrubbing system proved inadequate to deal with the rapid vapour release, and the flare was not alight, so that of the 35 t of isocyanate in the tank, some 23 t were released during the 2 h the safety valve was open.

The origin of the exothermic reaction was not clear at the time, but it was known that alkyl isocyanates would trimerise to trialkyl isocyanurates in the presence of various catalysts, would react with amines to form alkylureas, and were hydrolysed by water in presence of catalytic amounts of acids or bases, with evolution of carbon dioxide [2]. The key role of water has now been confirmed [3]. The Union Carbide report on the probable causes and course of the Bhopal disaster has been summarised [4,5]. Analysis of the residue in the distorted tank led to proposal of a mechanism, involving both water and chloroform as contaminants, to account for the detailed composition of the residue [6]. A detailed analysis of the many factors and failings which led to the ingress of water into the storage tank and to the subsequent disastrous large-scale vapour release has been presented [7]. Shortly after the event fatalities were estimated as 2,500, but such tolls do not shrink in retelling and figures up to 8,000 have since been given.

Bhopal exhibits several features of maladministration of chemical industry familiar to many who work in it on other continents. Construction of a fine chemical plant on a green field site soon causes local planners to regard the surrounding area as suitable for cheap high-density housing. As Trevor Kletz has reiterated in numerous books, add-on safety features, of which there were many, are a menace. If multiple, any one will be turned off as soon as it causes trouble or expense, and reliance be placed on the others which may be ill-designed and will, in any case, be later turned off in full confidence that the first is still working.

See related ORGANIC ISOCYANATES

0759a. Acetyl nitrite
[5813-49-0] **$C_2H_3NO_3$**

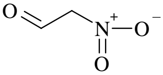


Francesconi, L. *et al., Gazz. Chim. Ital. [I]*, 1895, **34**, 439

An unstable liquid, decomposed by light, of which the vapour is violently explosive on mild heating.

See other ACYL NITRITES

0759b. Nitroacetaldehyde (Nitroethanal)
[44397-85-5] **$C_2H_3NO_3$**



Beilstein, Vol. 1, **III**, 2678

Decomposes on standing, explodes on contact with flame.

See other *C*-NITRO COMPOUNDS

0760. Poly(vinyl nitrate) (Poly(ethenyl nitrate))
[ ] **$(C_2H_3NO_3)_n$**

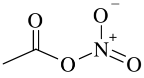
$(\text{-}CH_2CH(ONO_2)\text{-})_n$

Durgapal, U. C. *et al., Propellants, Explosives, Pyrotechnics*, 1995, **20**, 64

This compound, made by mild nitration of polyvinyl alcohol, is an explosive as shock sensitive as tetryl.

See other ALKYL NITRATES

0761. Acetyl nitrate
[591-09-3] **$C_2H_3NO_4$**



1. Pictet, A. *et al., Ber.*, 1907, **40**, 1164
2. Bordwell, F. G. *et al., J. Amer. Chem. Soc.*, 1960, **82**, 3588
3. Konig, W., *Angew. Chem.*, 1955, **667**, 517
4. Wibaut, J. P., *Chem. Weekbl.*, 1942, **39**, 534

Acetyl nitrate, readily formed above 0°C from acetic anhydride and conc. nitric acid, is thermally unstable and its solutions may decompose violently above 60°C (forming tetranitromethane, a powerful oxidant). The pure nitrate explodes violently on rapid heating to above 100°C [1]. Isolation before use as a nitrating agent at —10°C is not necessary, but the mixture must be preformed at 20—25° before cooling to —10°C to avoid violent reactions [2]. Spontaneous explosions of pure isolated material a few days old had been reported previously [3]. Spontaneous detonation of freshly distilled nitrate has also been recorded, as well as explosion on touching with a glass rod [4].

Ethyl 3,4-dihydroxybenzenesulfonate, Oleum

Dohmen, E. A. M. F. *et al., Chem. Weekbl.*, 1942, **39**, 447—448

Attempted nitration of the sulfonate in 20% oleum led to a violent explosion, probably from decomposition of the nitrate.

Mercury(II) oxide

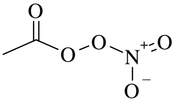
Chrétien, A. *et al., Compt. rend.*, 1945, **220**, 823

Acetyl nitrate explodes when mixed with red mercuric oxide, or other 'active' (catalytically) oxides.

See other ACYL NITRATES

0762. Peroxyacetyl nitrate (Acetyl nitro peroxide)

[2278-22-0] **$C_2H_3NO_5$**



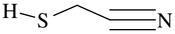
1. Stephens, E. R. *et al., J. Air Poll. Control Ass.*, 1969, **19**, 261—264
2. Stephens, E. R., *Anal. Chem.*, 1964, **36**, 928
3. Louw, R. *et al., J. Amer. Chem. Soc.*, 1975, **97**, 4396

Accidental production of the liquid nitrate during overcooled storage at 0°C of a rich mixture of the vapour with helium is thought to have caused a violent explosion [1]. Mixtures of up to 0.1 vol.% at 7 bar stored at 10°C or above are quite safe. During dilution with nitrogen of vapour samples in evacuated bulbs, slow pressurisation is necessary to avoid explosion [2]. It is extremely explosive and may only be handled in high dilution with nitrogen. The propionyl analogue is similarly explosive, but higher homologues less so [3].

See related ACYL NITRATES, PEROXYESTERS

0763. Mercaptoacetonitrile (Acetonitrilethiol)

[54524-31-1] **C_2H_3NS**



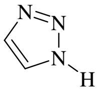
Mathias, E. *et al., J. Chem. Soc., Chem. Comm.*, 1981, 569—570

Great caution is necessary when handling conc. solutions or the solvent-free nitrile. Phosphoric acid stabilises it to some extent, but sudden foaming polymerisation may occur. Gaseous decomposition products may burst the container, even when kept in refrigerated storage.

See other CYANO COMPOUNDS, GAS EVOLUTION INCIDENTS

0764. 1,2,3-Triazole

[27070-49-1] **$C_2H_3N_3$**



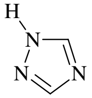
Baltzer, O. *et al., Ann.*, 1891, **262**, 320, 322

The vapour readily explodes if superheated (above 200°C), and the silver derivative explodes on heating.

See other TRIAZOLES

0765. 1,2,4-Triazole

[288-88-0] **$C_2H_3N_3$**



Energy of decomposition (in range 280—420°C) measured as 1.1kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other TRIAZOLES

0766. Vinyl azide

[7570-25-4] **$C_2H_3N_3$**

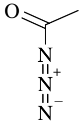
Wiley, R. H. *et al., J. Org. Chem.*, 1957, **22**, 995

A sample contained in a flask detonated when the ground joint was rotated. Literature statements that it is surprisingly stable are erroneous.

See other ORGANIC AZIDES

0767. Acetyl azide

[24156-53-4] **$C_2H_3N_3O$**



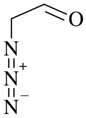
Smith, 1966, Vol. 2, 214

It is treacherously explosive.

See other ACYL AZIDES

0768. Azidoacetaldehyde

[67880-11-9] **$C_2H_3N_3O$**



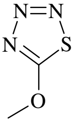
Forster, M. O. *et al., J. Chem. Soc.*, 1908, **93**, 1870

It decomposed with vigorous gas evolution below 80°C at 5 mbar. A preparative reaction mixture of chloroacetaldehyde hydrate and sodium azide had previously exploded mildly on heating in absence of added water.

See other 2-AZIDOCARBONYL COMPOUNDS

0769. 5-Methoxy-1,2,3,4-thiatriazole

[19155-52-3] **$C_2H_3N_3OS$**



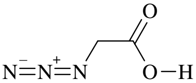
Jensen, K. A. *et al., Acta. Chem. Scand.*, 1964, **18**, 825

It explodes at ambient temperature, and its higher homologues are unstable.

See related TRIAZOLES

0770. Azidoacetic acid

[18523-48-3] **$C_2H_3N_3O_2$**



Iron, or Iron salts

Borowski, S. J., *Chem. Eng. News*, 1976, **54**(44), 5

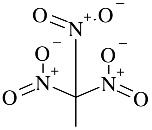
The pure acid is insensitive to shock at up to 175°C, and not explosively unstable at up to 250°C. In contrast, the presence of iron or its salts leads to rapid exothermic decomposition of the acid at 25°C, and explosion at 90°C or lower under strong illumination with visible light.

See Azidoacetyl chloride

See other 2-AZIDOCARBONYL COMPOUNDS, CATALYTIC IMPURITY INCIDENTS, IRRADIATION DECOMPOSITION INCIDENTS, ORGANIC ACIDS

0771. 1,1,1-Trinitroethane

[595-86-8] **$C_2H_3N_3O_6$**



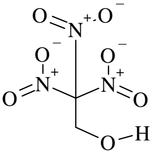
Mukhametshin, F. M., Russ. Pat. 515 378, 1976

Safety aspects of the preparation from halotrinitromethanes or tetranitromethane by treatment with methyl iodide are improved by use of an aprotic solvent (DMF, DMSO or HMPA) in diethyl ether or carbon tetrachloride at 30—60°C.

See other POLYNITROALKYL COMPOUNDS

0772a. 2,2,2-Trinitroethanol

[918-54-7] **$C_2H_3N_3O_7$**



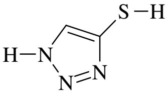
1. Marans, N. S. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 5329
2. Cochoy, R. E. *et al., J. Org. Chem.*, 1972, **37**, 3041
3. Shiino, K., *Chem. Abs.*, 1978, **88**, 104580

It is a moderately shock-sensitive explosive which has exploded during distillation [1]. A series of its esters, expected to be explosive, was prepared [2], and explosive ether and ester derivatives are reviewed [3].

See other POLYNITROALKYL COMPOUNDS

0772b. 1,2,3-Triazole-4-thiol (4-Mercaptotriazole)

[6440-06-8] **$C_2H_3N_3S$**



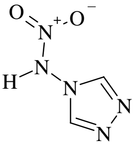
Lee S. & Robinson G., *Oxford Chemistry Primer 30, Process Development*, p20, Oxford, OUP, 1995

Stated to be explosive, but the sodium salt not (it probably exists as a thione, and there seems some confusion about the numbering)

See other TRIAZOLES

0773. 4-Nitroamino-1,2,4-triazole

[52096-16-9] **$C_2H_3N_5O_2$**



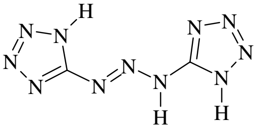
It explodes at the m.p., 72°C.

See entry N-AZOLIUM NITROIMIDATES

See other TRIAZOLES

0774. 1,3-Di(5-tetrazolyl)triazene

[56929-36-3] **$C_2H_3N_{11}$**



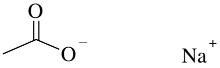
Hofman, K. A. *et al., Ber.*, 1910, **43**, 1869—1870

The barium salt explodes weakly on heating, and the copper salt and silver salt strongly on heating or friction.

See other TETRAZOLES, TRIAZENES

0775. Sodium acetate

[127-09-3] **$C_2H_3NaO_2$**



HCS 1980, 824

Diketene

See Diketene: Acids, etc.

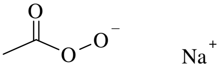
Potassium nitrate

See Potassium nitrate: Sodium acetate

See other METAL OXONON-METALLATES

0776. Sodium peroxyacetate (Sodium ethaneperoxoate)

[64057-57-4] **$C_2H_3NaO_3$**



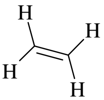
Humber, L. G., *J. Org. Chem.*, 1959, **24**, 1789

A sample of the dry salt exploded at room temperature.

See other METAL OXONON-METALLATES, PEROXOACID SALTS

†0777. Ethylene (Ethene)

[74-85-1] **C_2H_4**



FPA H17, 1973; *HCS 1980*, 458 (cryogenic liquid), 477 (cylinder gas)

1. Waterman, H. I. *et al., J. Inst. Petr. Tech.*, 1931, **17**, 505—510
2. Stull, 1977, 15—16
3. Conrad, D. *et al., Chem. Ing. Tech.*, 1975, **47**, 265 (summary of full paper)

4. Luft, G. *et al., Chem. Ing. Tech.*, 1978, **50**, 620—622
5. Lawrence, W. W. *et al., Loss Prev.*, 1967, **1**, 10—12
6. McKay, F. F. *et al., Hydrocarbon Proc.*, 1977, **56**(11), 487—494
7. Tanimoto, S., *Safety in Polyethylene Plants*, 1974, **2**, 14—21
8. Anon., *Oil Gas J.*, 1982, (1), 54
9. Watanabe, H. *et al., Chem. Abs.*, 1983, **98**, 218185
10. Brown, D. G., *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 1, M1—M10, Rugby, IChE, 1983
11. Britton, L. G., *Process Safety Progr.*, 1994, **13**(3), 128
12. Britton, L. G. *et al., Plant/Oper. Progr.*, 1986, **5**, 238—251
13. Gebauer, M. *et al.*, E. Ger. Pats DD 251 260—2, *Chem. Abs.*, 1988, **109**, 55464—6
14. Britton, L. G., *Process Safety Progr.*, 1996, **15**(3), 128
15. Black, D. E., *Int. Conf. Workshop Risk Anal. Process Saf.*, 1997, 461
16. Baca, B., *Chem. Abs.*, 2003, **139**, 201453n

Explosive decomposition in absence of air occurred at 350°C under a pressure of 170 bar [1]. An experimental investigation of the decomposition of ethylene (which is moderately endothermic, H_f°(g) +52.3 kJ/mol, 2.18 kJ/g) at 68 bar with high energy initiation (hot wire plus guncotton) gave results which were in close agreement with those calculated from thermodynamic data (exotherm of 4.33 kJ/g, flame temperature 1360°C, 6-fold pressure increase) [2]. The limiting pressures and temperatures for explosive decomposition of ethylene with electric initiation were determined in the ranges 100—250 bar and 120—250°C. Limiting conditions are much lower for high energy (exploding wire) initiation [3]. The study of spontaneous and initiated decomposition has been extended up to 5000 bar and 450°C, in the context of high pressure polymerisation of ethylene [4]. Previously, reaction parameters including effect of pipe size and presence of nitrogen as inert diluent upon the propagation of explosive decomposition had been studied using thermite initiation: 10 vol% of nitrogen markedly interferes with propagation [5].

Sudden pressurising with ethylene of part of an air-containing pipeline system from 1 to 88.5 bar led to adiabatic compressive heating and autoignition of the ethylene. The decomposition flame slowly propagated upstream into the main 30 cm pipeline and subsequent rupture of the latter occurred at an estimated wall temperature of 700—800°C. The AIT for ethylene in air at 1 bar is 492°C, but this falls with increase in pressure and could lie between 204 and 371°C at 68—102 bar, and the ethylene decomposition reaction may start at 315—371° within these pressure limits. Detonation was not, however, observed. Precautions against such incidents in ethylene installations are discussed [6]. In a published symposium mainly devoted to engineering aspects of large-scale polyethylene manufacture, this paper describes an extensive large-scale field experiment to determine the blast and destructive effects when various ethylene—air mixtures were detonated to simulate a compressor house explosion [7]. A fire and explosion in an ethylene separator was attributed to ingress of air which formed a catalytically active species which initiated exothermic polymerisation eventually leading to pipe rupture [8]. The decomposition of ethylene at 100—400 bar/20—149°C has been studied in detail [9]. An account of a decomposition incident at a high density polythene plant which was considered safe because it operated with ethylene diluted in a solvent is available [15].

In a review of low level ethylene decomposition since its discovery in 1842, the main factors are recognised as pressure—temperature—ignition relationships, heat balance in reaction zone and presence of impurities or contaminants. Case histories are discussed and safety practices and general recommendations are presented [10]. In a survey of incidents on high pressure ethylene plant, most appeared to involve overheating on molecular sieves in driers from polymerisation under conditions of reduced flow. Large pored sieves are not advisable [11]. An incident involving decomposition of liquid ethylene on an insufficiently cooled clay absorbent bed at an initial temperature not exceeding 180°C is reported [16]. In a review of the stability of ethylene at elevated pressures, the factors of thermal runaway, catalysis, influence of contaminants, and adsorptive heating, compressive ignition, and direct ignition are discussed, the effects of decomposition being described in terms of pressure and propagation [12]. A series of 3 patents describe start-up procedures to avoid explosive decomposition of ethylene during high-pressure polymerisation at 1600 bar using peroxide initiation. The procedures involve use of ethylene—hydrogen mixtures (6—30:1) with compression in several stages, interspersed with circulation through the reactor [13]. Another study of the slow deflagrative decomposition of ethene at around 300 bar to mostly methane, hydrogen and carbon is reported. Addition of hydrogen facilitates ignition, but not propagation, and increases the proportion of methane in the product. Hot spots, thence initiation, may develop over finely divided iron, starting from hydrogen reduction of rust from as low as 70°C [14].

Acetylene, Hydrogen
See Hydrogen (Gas): Acetylene, etc.

Air, Chlorine
Fujiwara, T. *et al.*, Jap. Pat., 74 32 841, 1974
During oxychlorination of ethylene to 1,2-dichloroethane, excess hydrogen chloride is used to maintain the reaction mixture outside the explosive limits.

Air, Polyethylene
Fonin, M. F. *et al., Chem. Abs.*, 1984, **101**, 111718
The solubility of ethylene in freshly prepared polyethylene, and its diffusion out of the latter were studied in relation to the formation of explosive ethylene—air mixtures in storage. Explosive mixtures may be formed, because the solubility of ethylene in its polymer (e.g. 1130 ppm w/w at 30°C) considerably exceeds the concentration (30 ppm at 30°C) necessary to exceed the lower explosive limit above the gas-containing polymer in closed storage, and the diffusion coefficient is also 30% higher than for aged polymer samples.

Aluminium chloride, Catalysts
Waterman, H. I. *et al., J. Inst. Pet.*, 1947, **33**, 254
Mixtures of ethylene and aluminium chloride, initially at 30—60 bar, rapidly heat and explode in presence of supported nickel catalysts, methyl chloride or nitromethane.
See Aluminium chloride: Alkenes

Aluminium chloride, Nitromethane
See Aluminium chloride—nitromethane: An alkene

Boron trioxide, Oxygen
Ts'olkovskii, T. I. *et al., Chem. Abs.*, 1979, **90**, 8511

AITs for ethylene—oxygen mixtures at 1 bar in stainless steel were reduced by 30—40°C by coating the vessel walls with boron trioxide.

Bromotrichloromethane MRH 1.21/90

Elsner, H. *et al., Angew. Chem.*, 1962, **74**, 253

Following a literature method for preparation of 1-bromo-3,3,3-trichloropropane, the reagents were being heated at 120°C/51 bar. During the fourth preparation, a violent explosion occurred.

See Halocarbons, below

Carbon tetrachloride MRH 1.55/85

Zakaznov, V. F. *et al., Khim. Prom.*, 1968, **8**, 584

Mixtures of ethylene and carbon tetrachloride can be initiated to explode at temperatures betwen 25 and 105°C and pressures of 30—80 bar, causing a six-fold pressure increase. At 100°C and 61 bar, explosion initiated in the gas phase propagated into the liquid phase. Increase of halocarbon conc. in the gas phase decreased the limiting decomposition pressure.

See Halocarbons, below

See also Dibenzoyl peroxide: Carbon tetrachloride, etc.

Chlorine

491M, 1975, 103

Interaction is explosive when catalysed by sunlight or UV irradiation, or in presence of mercury(I) oxide, mercury(II) oxide or silver oxide.

See Chlorine: Hydrocarbons

Chlorotrifluoroethylene

Colombo, P. *et al., J. Polymer Sci.*, 1963, **B1**(8), 435—436

Mixtures containing ratios of about 20:1 and 12:1 of ethylene:haloalkene undergoing polymerisation under gamma irradiation at 308 krad/h exploded violently after a total dose of 50 krad. Dose rate and haloalkene conc. were both involved in the initiation process.

See Halocarbons, below

Copper

Dunstan, A. E. *et al., J. Soc. Chem. Ind.*, 1932, **51**, 1321

Polymerisation of ethylene in presence of metallic copper becomes violent above a pressure of 54 bar at about 400°C, much carbon being deposited.

Halocarbons

See Bromotrichloromethane, and Carbon tetrachloride, and Chlorotrifluoroethylene, all above; Tetrafluoroethylene, below

Lithium

See Lithium: Ethylene

Molecular sieve

See MOLECULAR SIEVE INCIDENTS: Ethylene

Other reactants

Yoshida, 1980, 46

The MRH values calculated and given for 5 combinations are noted above and below.

Oxides of nitrogen

See Nitrogen oxide: Dienes, Oxygen

Ozone

See Ozone: Combustible gases, or: Ethylene

Steel-braced tyres

Anon., *CISHC Chem. Safety Summ.*, 1974—5, **45—46**, 2—3

Two hours after a road tanker had crashed, causing the load of liquid ethylene to leak, one of the tyres of the tanker burst and ignited the spill, eventually causing the whole tanker to explode. The tyre failed because it froze and became embrittled, and it is known that such failure of steel-braced tyres gives off showers of sparks. This could therefore be a common ignition source in cryogenic transportation spillage incidents.

See other IGNITION SOURCES

Tetrafluoroethylene

Coffman, D. D. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 492

A violent explosion occurred when a mixture of tetrafluoroethylene and excess ethylene was heated at 160°C and 480 bar. Traces of oxygen must be rigorously excluded. Other alkenes reacted smoothly.

See Oxygen (Gas): Tetrafluoroethylene

See also Halocarbons, above

Trifluoromethyl hypofluorite

See Trifluoromethyl hypofluorite: Hydrocarbons

Vinyl acetate

Albert J. *et al., Chem. Eng. Process*, 1998, **37**(1), 55

At pressures above 25 Mpa and temperatures above 250°C, vinyl acetate admixture destabilises ethylene and increases the maximum explosion pressure from its decomposition.

See other ALKENES

0778. Poly(ethylene)
[9002-88-4] **$(C_2H_4)_n$**

[671]

Experimental investigation of poly(ethylene) powder explosions.

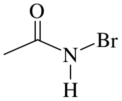
See entry DUST EXPLOSION INCIDENTS (reference 18)

0779. 1-Bromoaziridine
[19816-89-8] **C_2H_4BrN**

Graefe, A. F., *J. Amer. Chem. Soc.*, 1958, **80**, 3940

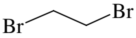
The compound is very unstable and always decomposes, sometimes explosively, during or shortly after distillation.
See other AZIRIDINES, *N*-HALOGEN COMPOUNDS

0780. *N*-Bromoacetamide
[79-15-2] **C_2H_4BrNO**



'Organic Positive Bromine Compounds', Brochure, Boulder (Co.) Arapahoe Chemicals Inc., 1962
It tends to decompose rapidly at elevated temperatures in presence of moisture and light.
See other *N*-HALOGEN COMPOUNDS

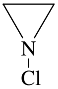
0781. 1,2-Dibromoethane (Ethylene dibromide)
[106-93-4] **$C_2H_4Br_2$**



HCS 1980, 365

Magnesium
See Magnesium: Halocarbons
See other HALOALKANES

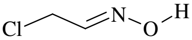
0782. 1-Chloroaziridine
[25167-31-1] **C_2H_4ClN**



1. Davies, C. S., *Chem. Eng. News*, 1964, **42**(8), 41
2. Graefe, A. F., *Chem. Eng. News*, 1958, **36**(43), 52

A sample of redistilled material exploded after keeping in an amber bottle at ambient temperature for 3 months [1]. A similar sample had exploded very violently when dropped [2].
See other AZIRIDINES, *N*-HALOGEN COMPOUNDS

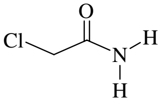
0783. Chloroacetaldehyde oxime
[51451-05-9] **C_2H_4ClNO**



1. Brintzinger, H. *et al., Chem. Ber.*, 1952, **85**, 345
2. Anon., *Chem. Eng. News*, 1993, **71**(34), 6

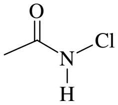
Vacuum distillation of the product at 61°C/27 mbar must be interrupted when a solid separates from the residue, to avoid an explosion [1]. A serious explosion occurred in a cooling loop containing the oxime and hydrochloric acid, during shutdown to clear a blockage elsewhere in a pesticide plant [2].
See Bromoacetone oxime
See other OXIMES
See related ALDEHYDES

0784. Chloroacetamide
[79-07-2] **C_2H_4ClNO**



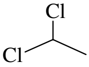
Energy of decomposition (in range 170—300°C) measured as 0.67kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

0785. *N*-Chloroacetamide
[598-49-2] **C_2H_4ClNO**



Muir, G. D., private comm., 1968
It has exploded during desiccation of the solid or during concentration of its chloroform solution. It may be purifed by pouring a solution in acetone into water and air-drying the product.
See other *N*-HALOGEN COMPOUNDS

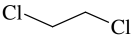
†0786. 1,1-Dichloroethane
[75-34-3] **$C_2H_4Cl_2$**



HCS 1980, 494

See other HALOALKANES

†0787. 1,2-Dichloroethane (Ethylene dichloride)
[107-06-2] **$C_2H_4Cl_2$**



(*MCA SD-18*, 1971); *NSC 350*, 1977; *FPA H77*, 1979; *HCS 1980*, 482

Chlorine
See Chlorine: 1,2-Dichloroethane

3-Dimethylaminopropylamine
491M, 1975, 171
After the amine was charged into a tank containing some residual wet halocarbon, a violent explosion occurred later. Subsequent investigation showed it was an extremely hazardous combination (as dehydrochlorination of the solvent would give acetylene).

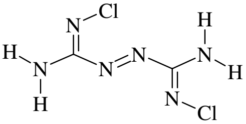
Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Halocarbons

Metals
Potassium: Halocarbons
See Aluminium: Halocarbons

Nitric acid
See Nitric acid: 1,2-Dichloroethane
See other HALOALKANES

0788. Azo-*N*-chloroformamidine

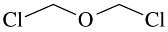
[502-98-7] **$C_2H_4Cl_2N_6$**



Braz, G. I. *et al., Chem. Abs.*, 1946, **40**, 2267.9
Decomposition is explosive at 155°C, and accelerated by contact with metals.
See other AZO COMPOUNDS, *N*-HALOGEN COMPOUNDS

†0789. Bis(chloromethyl) ether

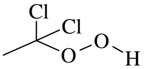
[542-88-1] **$C_2H_4Cl_2O$**



HCS 1980, 377; *RSC Lab. Hazards Data Sheet No. 46*, 1986

0790. 1,1-Dichloroethyl hydroperoxide

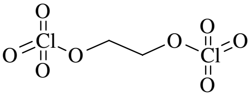
[90584-32-0] **$C_2H_4Cl_2O_2$**



Gäb, S. *et al., J. Org. Chem.*, 1984, **49**, 2714
Samples of the oil, either neat or as conc. solutions, rapidly decomposed exothermally on warming to ambient temperature. Although no explosions were experienced, caution is advised.

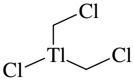
See Ozone: trans-2,3-Dichloro-2-butene
See other ALKYL HYDROPEROXIDES

0791. Ethylene diperchlorate
[52936-25-1] **$C_2H_4Cl_2O_8$**



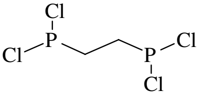
Schumacher, 1960, 214
A highly sensitive, violently explosive material, capable of detonation by addition of a few drops of water.
See other ALKYL PERCHLORATES

0792. Bis(chloromethyl)thallium chloride
[ ] **$C_2H_4Cl_3Tl$**



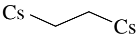
Yakubovich, A. Ya. *et al., Dokl. Akad. Nauk SSSR*, 1950, **3**, 957
An explosive solid of low stability.
See related ALKYLMETAL HALIDES

0793. 1,2-Bis(dichlorophosphino)ethane
[28240-69-9] **$C_2H_4Cl_4P_2$**



Chatt, J. *et al., J. Chem. Soc., Dalton Trans.*, 1985, 1131—1136
A modified method of preparation from ethylene, phosphorus trichloride and phosphorus in a stainless autoclave gives a highly pyrophoric reaction residue.
See related ALKYLHALOPHOSPHINES, PYROPHORIC MATERIALS

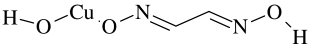
0794. Ethylenedicaesium
[65313-36-2] **$C_2H_4Cs_2$**



Leleu, *Cahiers*, 1977, (88), 366
Reacts violently with water.
See related ALKYLMETALS

0795. Hydroxycopper(II) glyoximate

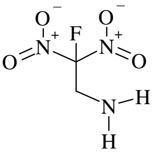
[63643-78-7] **$C_2H_4CuN_2O_3$**



Morpurgo, G. O. *et al., J. Chem. Soc., Dalton Trans.*, 1977, 746
The complex loses weight up to 140°C, then explodes.
See other HEAVY METAL DERIVATIVES
See related OXIMES

0796. 2-Fluoro-2,2-dinitroethylamine

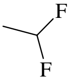
[18139-02-1] **$C_2H_4FN_3O_4$**



Adolph, H. G. *et al., J. Org. Chem.*, 1969, **34**, 47
Outstandingly explosive among fluorodinitromethyl compounds, samples stored neat at ambient temperatures regularly exploded within a few hours. Occasionally, concentrated solutions in dichloromethane have decomposed violently after long storage.
See other FLUORODINITROMETHYL COMPOUNDS

†0797. 1,1-Difluoroethane

[75-37-6] **$C_2H_4F_2$**

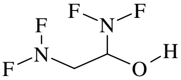


HCS 1980, 408 (cylinder)

See other HALOALKANES

0798. 1,2-Bis(difluoroamino)ethanol

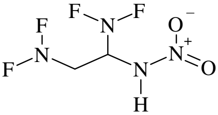
[13084-47-4] **$C_2H_4F_4N_2O$**



Reed. S. F., *J. Org. Chem.*, 1967, **32**, 2894
It is slightly more impact-sensitive than glyceryl trinitrate.
See other DIFLUOROAMINO COMPOUNDS

0799. 1,2-Bis(difluoroamino)-*N*-nitroethylamine

[18273-30-8] **$C_2H_4F_4N_4O_2$**



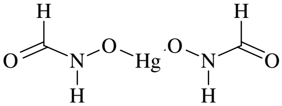
Tyler, W. E., US Pat. 3 344 167, 1967

The crude product tends to explode spontaneously on storage, though the triple-distilled material appears stable on prolonged storage. Generally, such nitroamines are unstable and explode at 75°C or above.

See other CATALYTIC IMPURITY INCIDENTS, DIFLUOROAMINO COMPOUNDS, N—NITRO COMPOUNDS

0800. Mercury(II) formohydroxamate

[ ] **$C_2H_4HgN_2O_4$**



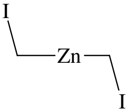
Urbanski, 1967, Vol. 3, 158

It possesses detonator properties.

See other MERCURY COMPOUNDS, N—O COMPOUNDS

0801. Bis(iodomethyl)zinc

[14399-53-2] **$C_2H_4I_2Zn$**



Dichloromethane

Charette, A. *Chem. Eng. News*, 1995, **73**(6), 2

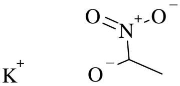
An explosion was twice experienced when working with a suspension of this compound in dichloromethane at near ambient temperature.

See Copper-zinc alloys: Diiodomethane, Ether

See also MAGNETIC STIRRERS

0802. Potassium 1-nitroethoxide

[ ] **$C_2H_4KNO_3$**

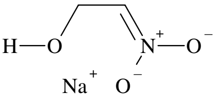


Meyer, V. *et al., Ber.*, 1872, **5**, 1032

The solid exploded on heating, and an aqueous solution sealed into a Carius tube exploded violently when the tube was cracked open with a red-hot glass rod. (The *aci*-salt may have been formed).
See other *C*-NITRO COMPOUNDS

0803. 2-Nitroethanol, sodium salt

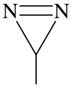
[2406-51-1] **$C_2H_4NNaO_3$**



Beilstein, **H1**, 339
Deflagrates at 120°C.
See other *C*-NITRO COMPOUNDS

0804. 3-Methyldiazirine

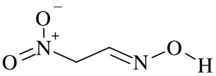
[765-31-1] **$C_2H_4N_2$**



Schmitz, E. *et al., Chem. Ber.*, 1962, **95**, 795
The gas explodes on heating.
See other DIAZIRINES

0805. 2-Nitroacetaldehyde oxime ('Methazonic acid')

[5653-21-4] **$C_2H_4N_2O_3$**

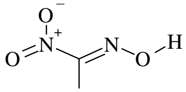


1. Sorbe, 1968, 149
2. Cooke, F., *Chem. Eng. News*, 1981, **59**(34), 3
3. Hoglen, D.K. *et al.*, Personal communication, 1997
4. Editor's comments

The oxime (an isomer of 'ethylnitrolic acid') decomposes gradually at ambient temperature, but explosively above 110°C [1]. The product from treatment of nitromethane with strong sodium hydroxide solution at 50°C, followed by acidification and ether extraction, gave, after vacuum evaporation, a residue which exploded when air was admitted. On this occasion, a weekend elapsed between alkali and acid treatments, and it seems possible that formation of fulminic acid derivatives may have occurred [2]. A 75 g sample of methazonic acid, from a preparation which had transiently overheated to 70°C, during the addition of nitromethane to sodium hydroxide solution, was stored for a week at —15°C, then allowed to warm to room temperature. Twelve hours later it spontaneously detonated, destroying a fume hood. There is no evident cause for this explosion [3]. It seems sensible to apply Occam's Razor, assume that methazonic acid is itself explosive, and cease to invoke impurities [4]. The salts of methazonic acid are also explosive.

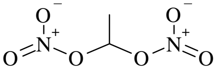
See Nitromethane: Acids, or Bases; Alkalis
See other OXIMES
See related ALDEHYDES

0806. 1-Nitro-1-oximinoethane ('Ethylnitrolic acid')
[600-26-0] **$C_2H_4N_2O_3$**



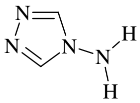
Sorbe, 1968, 147
An explosive solid, formally a nitro-oxime.
See other OXIMES

0807. Ethylidene dinitrate
[55044-04-7] **$C_2H_4N_2O_6$**



Kacmarek, A. J. *et al., J. Org. Chem.*, 1975, **40**, 1853
An analytical sample exploded in the hot zone of the combustion apparatus.
See Dinitrogen pentaoxide: Acetaldehyde
See other ALKYL NITRATES

0808a. 4-Amino-4*H*-1,2,4-triazole
[584-13-4] **$C_2H_4N_4$**

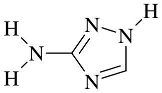


Preparative hazard

Tomann, J. *et al., Chem. Prum.*, 1987, **37**, 489—492
The title compound (with 66.5% nitrogen content) is prepared by condensing formylhydrazine (2 mols, with elimination of $2H_2O$) by heating to 170°C. During a pilot production run in a 500 l reactor, an explosion destroyed the vessel. The heat of decomposition of the compound was determined by thermal analysis as 1.5 kJ/g, with an energy of activation of 91 kJ/mol.
See other HIGH-NITROGEN COMPOUNDS, TRIAZOLES

0808b. 3-Amino-1,2,4-1*H*-triazole (1*H*-1,2,4-triazol-3-amine)

[61-82-5] **$C_2H_4N_4$**



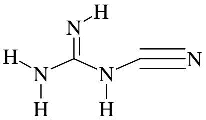
Weast, 2001, **5**1-60

A herbicide, thus handled on large scale in industry, this is the only triazole and simplest heterocyclamine featured in this table of ΔH_f° values. Someone must have had particular reason to establish its thermodynamic properties, though the Editor can find no incidents reported.

See other ENDOTHERMIC COMPOUNDS

0809. Cyanoguanidine ('Dicyanodiamide')

[461-58-5] **$C_2H_4N_4$**



HCS 1980, 386

Oxidants

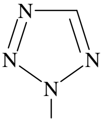
Baumann, J., *Chem. Ztg.*, 1920, **44**, 474

Mixtures of cyanoguanidine with ammonium nitrate, potassium chlorate, etc., were formerly proposed for use as powerful explosives.

See other CYANO COMPOUNDS, HIGH-NITROGEN COMPOUNDS

0810. 2-Methyltetrazole

[16681-78-0] **$C_2H_4N_4$**



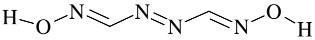
Aluminium hydride

See Aluminium hydride: Tetrazole derivatives

See other TETRAZOLES

0811. Azoformaldoxime

[74936-21-3] **$C_2H_4N_4O_2$**



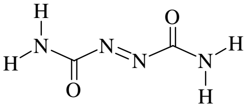
Armand, J. *et al., J. Chem. Res.; Synop.*, 1980, 304; *Microf.* 1980, 3853—3869

The dioxime exploded on melting, as did the cyclised isomeric triazole derivative, 1-hydroxy-2-hydroxylamino-1,3,4-triazole.

See other AZO COMPOUNDS, N—O COMPOUNDS, OXIMES

0812. Azoformamide (Azodicarboxamide)

[123-77-3] **$C_2H_4N_4O_2$**



Whitmore, M. W. *et al., J. Loss Prev.*, 1993, **6**(3), 169

An 850 kg batch of a slightly doped form of azodicarbonamide exploded violently, with a TNT equivalence of 3.3 kg, 5 minutes after sampling at the end of drying. The probable initial temperature was 65°C, the lowest self accelerating decomposition temperature 90°C, and such decomposition is not explosive. Full explosibility tests, including detonability, had shown no hazard. Further study demonstrated that slightly contained azodicarboxamide, thermally initiated at the bottom of a column or conical vessel could explode even at the 5 kg scale. The above TNT equivalence corresponds to decomposition of 4% of the available charge. The cause of the presumptive hot spot is unknown.

Energy of decomposition (in range 160—230°C) measured as 1.36 kJ/g by DSC, and T_{ait24} was determined as 120°C by adiabatic Dewar tests, with an apparent energy of activation of 131 kJ/mol.

See entry BLOWING AGENTS, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

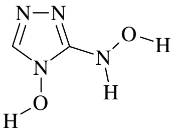
Potassium bromate

See Potassium bromate: Azoformamide

See other AZO COMPOUNDS

0813. 1-Hydroxy-2-hydroxylamino-1,3,4-triazole

[76002-04-5] **$C_2H_4N_4O_2$**



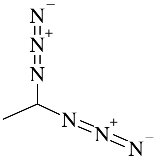
Armand, J. *et al., J. Chem Res.; Synop.*, 1980, 304; *Microf.*, 1980, 3853—3869

The triazole exploded on melting, as did the isomeric azoformaldoxime, from which it is prepared by cyclisation.

See other HIGH-NITROGEN COMPOUNDS, N—O COMPOUNDS, TRIAZOLES

0814. 1,1-Diazidoethane

[67880-20-0] **$C_2H_4N_6$**



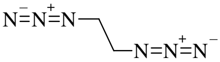
Forster, M. O. *et al., J. Chem. Soc.*, 1908, **93**, 1070

The extreme instability and explosive behaviour of this diazide caused work on other *gem*-diazides to be abandoned.

See other ORGANIC AZIDES

0815. 1,2-Diazidoethane

[629-13-0] **$C_2H_4N_6$**



Alone, or Sulfuric acid

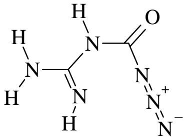
Forster, M. O. *et al., J. Chem. Soc.*, 1908, **93**, 1070

Though less unstable than the 1,1-isomer (next above), it explodes on heating, and irreproducibly in contact with sulfuric acid.

See other ORGANIC AZIDES

0816. Azidocarbonylguanidine

[54567-24-7] **$C_2H_4N_6O$**



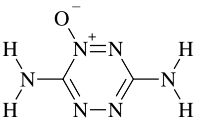
Thiele, J. *et al., Ann.*, 1898, **303**, 93

It explodes violently on rapid heating.

See related ACYL AZIDES

0817. 3,6-Diamino-1,2,4,5-tetrazine-1-oxide

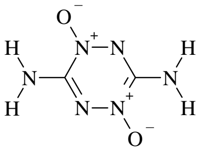
[153757-93-8] **$C_2H_4N_6O$**



See 3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide

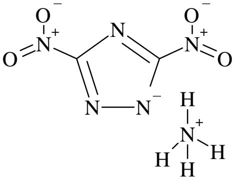
See also AMINE OXIDES
See other HIGH-NITROGEN COMPOUNDS

0818. 3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide
[153757-93-8] **$C_2H_4N_6O_2$**



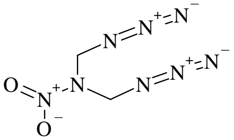
Coburn, M. D. *et al., J. Heterocycl. Chem.*, 1993, **30**(6), 1593
This, the mono-oxide and the 3-amino-6-nitro-2,4-dioxide are all explosives to be handled with care. All are thermally stable well above 100°C.
See also AMINE OXIDES
See other HIGH-NITROGEN COMPOUNDS

0819. Ammonium 3,5-dinitro-1,2,4-triazolide
[76556-13-3] **$C_2H_4N_6O_4$**



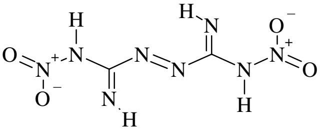
Selig, W., *Propellants Explos.*, 1981, **6**, 96—98
It is an explosive.
See other TRIAZOLES

0820. 1,3-Diazido-2-nitroazapropane (*N,N*-Bis(azidomethyl)nitric amide))
[67362-62-3] **$C_2H_4N_8O_2$**



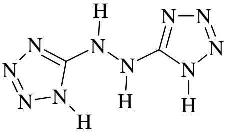
Flanagan, J. E. *et al.*, US Pat. 4 085 123, 1978
It is useful as a high energy plasticiser for propellants.
See other N—NITRO COMPOUNDS, ORGANIC AZIDES

0821. Azo-*N*-nitroformamidine
[53144-64-2] **$C_2H_4N_8O_4$**



Wright, G. F., *Can. J. Chem.*, 1952, **30**, 64
Explosive decomposition at 165°C.
See other AZO COMPOUNDS, N—NITRO COMPOUNDS

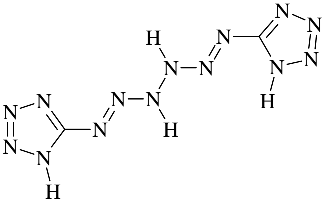
0822. 5,5′-Hydrazotetrazole
[74999-19-2] **$C_2H_4N_{10}$**



1. Thiele, J. *et al., Ann.*, 1898, **303**, 66
2. Reddy, G. O., *J. Haz. Mat.*, 1984, **9**, 291—303

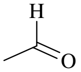
It explodes without melting when heated [1]. The title compound and its barium, lead(II), and mercury(II) salts were studied by DTA and DSC techniques. The lead salt is the least stable and most powerful primary explosive of the 4 compounds [2].
See other HIGH-NITROGEN COMPOUNDS, TETRAZOLES

0823. 1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene
[68594-19-4] **$C_2H_4N_{14}$**



Hofman, K. A. *et al., Ber.*, 1911, **44**, 2953
This very high-nitrogen compound (87.5%) explodes violently on pressing with a glass rod, or on heating to 90°C.
See other HIGH-NITROGEN COMPOUNDS, TETRAZOLES

†0824. Acetaldehyde (Ethanal)
[75-07-0] **C_2H_4O**



(*MCA SD-43*, 1952); *FPA H29*, 1974; *HCS 1980*, 97; *RSC Lab. Hazards Data Sheet No. 38*, 1985

1. White, A. G. *et al., J. Soc. Chem. Ind.*, 1950, **69**, 206
2. Vervalin, 1973, 90—91
3. Garbuzynk, T. A., *Chem. Abs.*, 1978, **89**, 131835; 1989, **111**, 117216b
4. Nalbandyan, A. B. *et al., Prog. Astronaut. Aeronaut.*, 1988, **113**, 58; *Chem. Abs.*, 1989, **111**, 22912; *Khim. Fiz.*, 1988, **7**(12), 1709; *Chem. Abs.*, 1989, **111**, 56791

(The MCA Data Sheet describes acetaldehyde as extremely or violently reactive with: acid anhydrides, alcohols, halogens, ketones, phenols, amines, ammonia, hydrogen cyanide or hydrogen sulfide). Mixtures of 30—60% of acetaldehyde vapour with air (or 60—80% with oxygen) may ignite on surfaces at 176 and 105°C, respectively, owing to formation and subsequent violent decomposition of peroxyacetic acid [1]. Acetaldehyde vapour leaking into a building equipped only with flameproof electrical equipment nevertheless ignited, possibly on contact with rusted steel, corroded aluminium or hot steam lines [2]. The minimum AIT (130°C) for acetaldehyde in air mixtures is at 55—57 vol.% of aldehyde. The effect of presence of acetone or methane upon AIT was studied, they inhibit ignition during the oxidation to peroxyacetic acid; the AIT is surface sensitive and may be as low as 80°C in quartz [3]. The mechanism of this ignition has been studied [4], it is catalysed by peroxy-acids on the surface of the reactor.

See other CATALYTIC IMPURITY INCIDENTS

Acetic acid MRH 1.13/tr.

MCA Case History No. 1764

A drum contaminated with acetic acid was filled with acetaldehyde. The ensuing exothermic polymerisation reaction caused a mild eruption lasting several hours.

Cobalt acetate, Oxygen

1. Phillips, B. *et al. J. Amer. Chem. Soc.*, 1957, **79**, 5982
2. Bloomfield, G. F. *et al., J. Soc. Chem. Ind.*, 1935, **54**, 129T

Oxygenation of acetaldehyde in presence of cobalt acetate at —20°C caused precipitation of 1-hydroxyethyl peroxyacetate (acetaldehyde hemi-peracetate), which exploded violently on stirring [1]. Ozone or UV light also catalyses the autoxidation [2].

Desiccants, Hydrogen peroxide

See Hydrogen peroxide: Acetaldehyde, Desiccants

Dinitrogen pentaoxide

See Dinitrogen pentaoxide: Acetaldehyde

Halocarbons

Jones, J. C. *et al., Combust. Flame*, 1983, **52**, 211—213

Cool flame behaviour of acetaldehyde is apparently eliminated by *tert*-butyl bromide, and reduced by methyl iodide.

Hydrogen peroxide MRH 6.27/79

See Hydrogen peroxide: Oxygenated compounds

Mercury(II) oxosalts

Sorbe, 1968, 97

Some of the products of interaction of acetaldehyde and mercury(II) chlorate or mercury(II) perchlorate are highly explosive and extremely shock-sensitive.

See Chloratomercurio(formyl)methylenemercury(II)

Metals

Sorbe, 1968, 103

Impure material will polymerise readily in presence of trace metals (iron) or acids.

See Sulfuric acid, below

See other CATALYTIC IMPURITY INCIDENTS

Other reactants

Yoshida, 1980, 17

MRH values calculated for 18 combinations, largely with oxidants, are given.

Oxygen MRH 8.66/64

1. *MCA Case History No. 117*
2. Armstamyan, A. M. *et al., Chem. Abs.*, 1984, **101**, 194603

Oxygen leaked into the free space in an acetaldehyde storage tank normally purged with nitrogen. Accelerating exothermic oxidation led to detonation [1]. The self-ignition temperature of acetaldehyde—oxygen mixtures depends on dimensions of the reactor and the partial pressure of peracetic acid accumulated on the walls. Spontaneous ignition temperatures of 71—73°C were observed [2].

Silver nitrate

See Silver nitrate: Acetaldehyde

Sulfuric acid MRH 1.34/43

Sorbe, 1968, 103

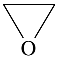
Acetaldehyde is polymerised violently by the conc. acid.

See Metals, above

See other ALDEHYDES, PEROXIDISABLE COMPOUNDS, POLYMERISATION INCIDENTS

†0825. Ethylene oxide (Oxirane)

[75-21-8] C_2H_4O



(*MCA SD-38*, 1971); *FPA H32*, 1974; *HCS 1980*, 486; *RSC Lab. Hazard Data Sheet No. 2*, 1982

1. *Guidelines for Bulk Handling of Ethylene Oxide, London, CIA, 1983*
2. Hess, L. G. *et al., Ind. Eng. Chem.*, 1950, **42**, 1251
3. Burgoyne, J. H. *et al.,Proc. 1st Symp. Chem. Proc. Hazards*, Symp. Ser. No. 7, 30—36, London, IChE, 1960; *Proc. 3rd Symp. Chem. Proc. Hazards*, Symp. Ser. No. 25, 1—7, London,IChE, 1967
4. *MCA SD-38*, 1971

5. *MCA Case History No. 1666*
6. Harmon, 1974, 2.9
7. Heuser, S. G. B., *Chem. Brit.*, 1977, **13**, 317
8. Pogany, G. A., *Chem. & Ind.*, 1979, 16—21
9. Pesetsky, B. *et al., Loss Prev.*, 1980, **13**, 123—131
10. Pesetsky, B. *et al., Loss Prev.*, 1980, **13**, 132—141
11. Chen, L. D. *et al., Combust. Flame*, 1981, **40**, 13—28
12. *See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
13. Loeffler U., *Prax. Sicherheitstech.*, 1997, **4**, 31
14. Britton, L. G., *Plant/Oper. Progr.*, 1990, **9**(2), 75
15. Gustin, J_L., *Hazards XV, Inst. Chem. Eng. Symp. Ser.*, 2000, **147**, 251
16. Ethylene Oxide, User's Guide, 1999, www.ethyleneoxide.com
17. Britton, L. G., *Process Safety Progr.*, 2000, **19**(4), 199
18. Levin, M. E. *J. Haz. Mat.*, 2003, **104**(1-3), 227
19. Viera, G. A. *et al., Chem. Eng. Progress*, 1993, **89**(8), 66
20. Anon., *Loss Prev. Bull.*, 1991, **100**, 1; Mellin, B. E., *ibid.*, 13

The detailed code of practice [1] serves as a comprehensive guide to the industrial use of ethylene oxide, replacing the US Safety Data Sheet withdrawn in 1980. A consortium of US producers has more recently prepared a very thorough guide to hazards, properies and handling, which can be accessed via the internet [16]. Ethylene oxide vapour may readily be initiated into explosive decomposition in absence of air, and storage and handling requirements were detailed [2]. Explosive decomposition may be suppressed by many diluents, not necessarily inert [3]. Propylene oxide has been suggested as an ethylene oxide diluent. Under some circumstances it suppresses decomposition of the ethylene oxide more effectively than does nitrogen Under others, it decomposes also, so increasing hazard [17]. Metal fittings containing copper, silver, mercury or magnesium should not be used in ethylene oxide service, since traces of acetylene in the oxide could produce metal acetylides capable of detonating the vapour [4]. Ethylene oxide exposed to heating and subsequently cooled (e.g. by exposure to fire conditions) may continue to polymerise exothermically, leading to container pressurisation and explosion. A mechanism consistent with several observed incidents is proposed [5]. Presence of hot spots in processing plants is identified as a particular hazard [6]. These can be generated by the polymerisation/autoxidation of leaks absorbed onto lagging material, with devastating results [13, 20], or by catalysis of decomposition especially by γ-ferric oxide and γ-FeO(OH), though other iron oxides are also effective [18,19]. Appropriate column packing can inhibit propagation of ethylene oxide decomposition from hot spots in ethylene oxide stills [13]. Combustion properties, including ignition of leaks onto packing are reviewed thoroughly. The autoignition temperature may be as low as 140°C in presence of rust. Aerosols, detonated rather than ignited, are used in fuel/air weapons, giving a TNT equivalence of 2.4 kg/kg. Under conditions of ignition and deflagration TNT equivalence is more like zero [14]. Liquid phase decomposition, previously thought not possible, was observed under conditions of temperature and pressure outside the normal working range with different submerged igniter wires, and a mechanism is discussed [9]. The use of methane as a diluent for ethylene oxide has been studied in detail [10]. The decomposition threshold temperature for ethylene oxide has been related to pressure, ignition source and geometry of the containment vessel, pressure having the greatest effect [11]. The energy of decomposition (in range 320—490°C) has been revised to 1.516 kJ/g [12].

Hazards attendant on use of ethylene oxide in steriliser chambers arise from difficulties in its subsequent removal by evacuation procedures, owing to its ready absorption or adsorption by the treated material. Even after 2 evacuation cycles the oxide may still be present. Safety is ensured by using the oxide diluted with up to 90% of Freon or carbon dioxide. If high concentrations of oxide are used, an inert gas purge between cycles is essential [7]. The main factors in safe handling and use on laboratory or small pilot plant scales have been identified [8]. Safe operation of ethoxylation processes on industrial scale is discussed, with case histories [15].

See also ENVIRONMENTALISM, VIOLENT POLYMERISATION; INSULATION
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other POLYMERISATION INCIDENTS

Air, Bromomethane

Baratov, A. N. *et al.*, p.24 of BLL translation (628.74, issued 1966) of Russian book on ‘Fire Prevention and Firefighting Symposium’. The addition of bromomethane to ethylene oxide (used for germicidal sterilising) to reduce the risk of explosion is relatively ineffective, the inhibiting concentration being 31.2, as against 5.8 for hexane and 13.5 vol.% for hydrogen.

Air, Ethylene

See Oxygen, below

Alkanethiols, or An alcohol

1. Meigs, D. P., *Chem. Eng. News*, 1942, **20**, 1318
2. Personal experience (PGU)

Autoclave reactions involving ethylene oxide with alkanethiols or an (unspecified) alcohol went out of control and exploded violently. Similar previous reactions had been uneventful [1]. An arenethiol was being reacted with ethylene oxide under catalysis by a fraction of a percent of sodium hydroxide (solid) dissolved in the thiol to which the oxirane was slowly charged. After an initial exotherm a white solid precipitated, the exotherm died away and later resumed, with dissolution of the solid, the reaction then running out of control from the backlog of charged oxirane [2].

Ammonia

1. *MCA Case History No. 792*
2. Troyan, J. E. *et al., Loss Prev.*, 1968, **2**, 125—130
3. Stull, 1977, 26—27

Accidental contamination by aqueous ammonia of an ethylene oxide feed tank containing 22 t caused violent polymerisation which ruptured the tank and led to a devastating vapour cloud explosion [1,2]. The close similarity to other base-catalysed incidents was stressed [3].

See Contaminants, and Trimethylamine, both below
See other POLYMERISATION INCIDENTS, RUNAWAY REACTIONS, VIOLENT POLYMERISATION

Contaminants

1. Gupta, A. K., *J. Soc. Chem. Ind.*, 1949, **68**, 179
2. Stull, 1977, 26—27
3. Freeder, B. G. *et al., J. Loss Prev. Process Ind.*, 1988, **1**, 164—168

Accidental contamination of a 90 kg cylinder of ethylene oxide with a little sodium hydroxide solution led to explosive failure of the cylinder over 8 hours later [1]. Based on later studies of the kinetics and heat release of the polycondensation reaction, it was estimated that after 8 hours and 1 min, some 12.7% of the oxide had condensed with an increase in temperature from 20 to 100°C. At this point the heat release rate was calculated to be 2.1 MJ/min, and 100 s later the temperature and heat release rate would be 160° and 1.67 MJ/s respectively, with 28% condensation. Complete reaction would have been attained some 16 s later at a temperature of 700°C [2]. Precautions designed to prevent explosive polymerisation of ethylene oxide are discussed, including rigid exclusion of acids; covalent halides, such as aluminium chloride, iron(III) chloride, tin(IV) chloride; basic materials like alkali hydroxides, ammonia, amines, metallic potassium; and catalytically active solids such as aluminium oxide, iron oxide, or rust [1]. A comparative study of the runaway exothermic polymerisation of ethylene oxide and of propylene oxide by 10 wt% of solutions of sodium hydroxide of various concentrations has been done using ARC. Results below show onset temperatures/corrected adiabatic exotherm/maximum pressure attained; and heat of polymerisation for the least (0.125 M) and most (1 M) concentrated alkali solutions used as catalysts.

EO 55.0, 22,5°C/439, 415°/40.5, 44.6 bar; 1.06, 1.0 kJ/g.
PO 91, 53°/451, 452°/26.6, 20.9 bar; 1.09, 1.1 kJ/g

The more reactive ethylene oxide clearly shows much higher self-heating rates and hazard potential than its higher homologue, though more detailed work is needed to quantify the differences [3].

See Ammonia, above; Trimethylamine, below

See other CATALYTIC IMPURITY INCIDENTS, POLYCONDENSATION REACTION INCIDENTS, POLYMERISATION INCIDENTS

Dinitrogen pentaoxide

See Dinitrogen pentaoxide: Strained ring heterocycles

Glycerol

Anon., *Loss Prev. Bull.*, 1979, (028), 92—93

Glycerol was to be ethoxylated at 115—125°C in a circulating reaction system with separate reactor, heat exchanger and catalyst units. The valve at the base of the reactor was still closed, but an inoperative flow indicator failed to indicate absence of circulation and a total of 3 tonnes of the oxide, plus glycerol, was charged to the reactor. Upon subsequent opening of the valve, the reaction mixture passed through the heater, now at 200°C, and a runaway reaction developed, the reactor burst and an explosion followed.

See other RUNAWAY REACTIONS

Iron(III) hexacyanoferrate(4—) (‘Iron blue pigment’)

See Iron(III) hexacyanoferrate(4—): Ethylene oxide

Lagging materials

Hilado, C. J., *J. Fire Flamm.*, 1974, **5**, 321—326

The self-heating temperature (effectively the AIT) of a 50:50 mixture of ethylene oxide and air is reduced from 456°C on passage through various thermal insulation (lagging) materials to 251—416°C, depending on the particular material (of which 13 were tested).

Magnesium perchlorate

See Magnesium perchlorate: Ethylene oxide

4-Methoxybenzenelithium

Taylor, D. A. H., personal comunication, 1993

Oxirane was added to the organolithium (probably in ether solution) at a temperature perhaps —40°C. The mixture was then allowed to warm up, went out of control and distributed itself widely. Presumably too much ethylene oxide had accumulated because of sluggish reaction at the low temperature.

See Alkanethiols, above

3-Nitroaniline

Anon., *Angew. Chem. (Nachr.)*, 1958, **70**, 150

Interaction of the two compounds in an autoclave at 150—160°C is described as safe in Swiss Pat. 171 721. During careful repetition of the reaction with stepwise heating, an autoclave exploded at 130°C.

Nitrogen

Grosse-Wortmann, H., *Chem. Ing. Tech.*, 1970, **42**, 85—86

Concentration boundaries for explosive decomposition of the oxide and its mixtures with nitrogen at elevated temperatures and pressures are presented graphically.

Other reactants

Yoshida, 1980, 47

MRH values calculated for 13 combinations with oxidants are given.

Oxygen

Griffiths, R. F. *et al., Proc. 18th Int. Combust. Symp.*, 1981, 893—901

If rapid compression of dilute ethylene oxide vapours occurs, ignition and/or decomposition may occur. Thus 5% of oxide in argon will ignite if compressed more than 11-fold, and presence of traces of oxygen enhances the effect. Even 1% or less of ethylene in the oxide in air may be hazardous if modest but rapid compression occurs.

Polyhydric alcohol, Propylene oxide

Vervalin, 1973, 82

A polyether-alcohol, prepared by co-condensation of ethylene oxide and propylene oxide with a polyhydric alcohol, was stored at above 100°C and exposed to air via a vent line. After 10—15 h, violent decomposition occurred, rupturing the vessel. It was subsequently found that exothermic oxidation of the product occurred above 100°C, and that at 300°C a rapid exothermic reaction set in, accompanied by vigorous gas evolution.

See other GAS EVOLUTION INCIDENTS

Pyridine, Sulfur dioxide

Nolan, 1983, Case History 151

Ethylene sulfite is prepared from ethylene oxide, pyridine, and sulfur dioxide in excess to prevent polymerisation of ethylene oxide. Use of a deficiency of sulfur dioxide led to rupture of a reactor from that cause.

Sodium hydroxide

See Contaminants, above

Sucroglyceride

1. Slade, R. C., *Chem. Brit.*, 1977, **13**, 317
2. Parker, K. J., private comm., 1977

During ethoxylation of the glyceride by stirring and heating to 120°C with excess ethylene oxide in an autoclave fitted with a 300 bar bursting disc [1], exothermic reaction occurred, usually causing an increase in temperature to 190°C (even with ice cooling applied) when large excesses were used. In one such attempt, an operating error led to the initial ethylene oxide charge being distilled out of the autoclave via an open vent valve, and the dry residue being heated to a temperature considerably above the 100°C indicated by the (unwetted) pocketed thermocouple. After cooling, more oxide was added and the preparation was continued. At an indicated temperature of 126°C and a pressure reading above 10 bar, it was decided to cool the autoclave to moderate the accelerating reaction. At this point, the rapidly increasing pressure and temperature caused the autoclave lid bolts to stretch and relieve the explosive reaction [2]. It is surmised that during the 'false start' of the reaction, a layer of the sucroglyceride became distributed as a paste round the heated autoclave wall, and was then overheated, forming an insulating layer on the autoclave wall. After more ethylene oxide was added and heating restarted, the indicated liquid temperature (126°C) would be far below that of the heated autoclave wall behind the insulating layer of thermally degraded solid. Dissolution of the inner layers of solid in the hot ethylene oxide may have exposed a hot spot which initiated thermal decomposition. Additionally or alternatively, local concentrations of alkali arising from thermal decomposition of potassium soaps present as impurity in the sucroglyceride may have initiated exothermic polymerisation of the oxide.

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Trimethylamine

1. Anon., *BCISC Quart. Safety Summ.*, 1966, **37**, 44
2. Anon., *Chem. Trade J.*, 1956, **138**, 1376

Accidental contamination of a large ethylene oxide feed-cylinder by reaction liquor containing trimethylamine caused the cylinder to explode 18 h later. Contamination was possible because of a faulty pressure gauge and suck-back of froth from above the liquid level [1]. A similar incident had occurred previously [2].

See Ammonia, and Contaminants, both above

Water

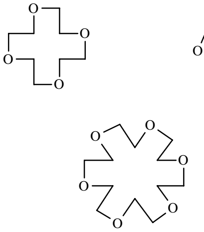
Vanderwater, R. G., *Chem. Eng. Progress*, 1989, **85**(12), 16

A supposedly empty tankwagon, which may have still held 12 tonnes of oxirane, was filled with water as the first stage of a cleaning process and the valves then closed. Several hours later, an explosion shattered the tank, sending parts up to 600 metres distance. It appears that filling will not have given complete mixing but left an oxirane layer on top of the water, which would be heated, but not mixed, by reaction with water at the interface, possibly aided by catalysis at sites of corrosion. There should have been enough water to act as a heat sink had it mixed. Explosion appears to have taken place within the supernatant ethylene oxide layer.

See other CORROSION INCIDENTS, 1,2-EPOXIDES

0826. Cyclic poly(ethylene oxides) ('Crown ethers')

[294-93-9] (*n* = 4) [33100-27-5] (*n* = 5) [17455-13-9] (*n* = 6) **$(C_2H_4O)_n$**

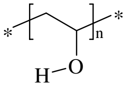


Bromoform, Potassium hydroxide

See Bromoform: Cyclic poly(ethylene oxides), etc.

0827. Poly(vinyl alcohol)

[9002-89-5] **$(C_2H_4O)_n$**

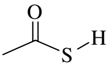


Energy of decomposition (in range 125—430°C) measured as 0.59 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

†0828. Thiolacetic acid

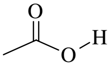
[507-09-5] **C_2H_4OS**



See other ORGANIC ACIDS

0829. Acetic acid (Ethanoic acid)

[64-19-7] **$C_2H_4O_2$**



(*MCA SD-41*, 1951); *NSC 410*, 1979; *FPA H120*, 1983; *HCS 1980*, 99

Acetaldehyde
See Acetaldehyde: Acetic acid

Acetic anhydride, Water
See Acetic anhydride: Acetic acid, Water

5-Azidotetrazole
See 5-Azidotetrazole: Alone, or Acetic acid

Other reactants
Yoshida, 1980, 121
MRH values calculated for 15 combinations are given.

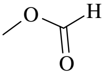
Oxidants	MRH values show % of oxidant
See Bromine pentafluoride: Hydrogen-containing materials	
Chromium trioxide: Acetic acid	MRH 2.17/12
Hydrogen peroxide: Acetic acid	MRH 5.10/69
Potassium permanganate: Acetic acid	MRH 2.34/84
Sodium peroxide: Acetic acid	MRH 2.80/84

Phosphorus trichloride
See Phosphorus trichloride: Carboxylic acids (references 1,2)

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids
See other ORGANIC ACIDS

†0830. Methyl formate (Methyl methanoate)

[107-31-3] **$C_2H_4O_2$**

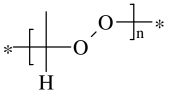


HCS 1980, 653

Methanol, Sodium methoxide
Pond, D. M., *Chem. Eng. News*, 1982, **60**(37), 43
The crude product of reaction of methanol and carbon monoxide at 100°C/70 bar in presence of 0.5% of sodium methoxide was discharged after cooling into a storage bottle, which burst 4 h later. This was attributed to extreme instability of the ester in presence of the base, leading to the reverse reaction with vigorous evolution of carbon monoxide. Immediate neutralisation of the reaction mixture would prevent the decomposition, which also occurs with ethyl formate and base.
See other GAS EVOLUTION INCIDENTS

0831. Poly(ethylidene peroxide)

[ ] **$(C_2H_4O_2)_n$**



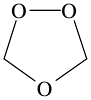
Rieche, A. *et al., Angew. Chem.*, 1936, **49**, 101

The highly explosive polyperoxide is present in peroxidised diethyl ether and has been responsible for many accidents during distillation of the solvent.

See other POLYPEROXIDES

0832. Ethylene ozonide (1,2,4-Trioxolane)

[289-14-5] **$C_2H_4O_3$**



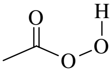
1. Harries, C. *et al., Ber.*, 1909, **42**, 3305
2. Briner, E. *et al., Helv. Chim. Acta*, 1921, **12**, 154
3. Criegee, R., *Angew. Chem.*, 1958, **65**, 398—399

It explodes very violently on heating, friction or shock [1]. Stable at 0°C, but often decomposes explosively at ambient temperature [2]. Pouring the liquid from one vessel to another initiated a violent explosion [3].

See other OZONIDES

0833. Peroxyacetic acid (Ethaneperoxoic acid)

[79-21-0] **$C_2H_4O_3$**



FPA H89, 1980; *HCS 1980*, 720 (40% solution in acetic acid)

1. Swern, D., *Chem. Rev.*, 1949, **45**, 7
2. Davies, 1961, 56
3. Phillips, B. *et al., J. Org. Chem.*, 1959, **23**, 1823
4. Anon., *Angew. Chem. (Nachr.)*, 1957, **5**, 178
5. Smith, I. C. P., private comm., 1973
6. *MCA Case History No. 1804*
7. Slattery, G. H., US Pat. 4 137 256, 1979

It is insensitive to impact but explodes violently at 110°C [1]. The solid acid has exploded at —20°C [2]. Safe procedures (on basis of detonability experiments) for preparation of anhydrous peracetic acid solutions in chloroform or ester solvents have been detailed [3]. However, a case of explosion on impact has been recorded [4]. During vacuum distillation, turning a ground glass stopcock in contact with the liquid initiated a violent explosion, but the grease may have been involved as well as friction [5]. During a pilot-scale preparation of a solution of the acid by adding acetic anhydride slowly to 90% hydrogen peroxide in dichloromethane, an explosion of great violence occurred. Subsequent investigation revealed that during the early stages of the addition a 2-phase system existed, which was difficult to detect because of closely similar densities and refractive indices. The peroxide-rich phase became extremely shock-sensitive when between 10 and 30% of the anhydride had been added [6]. A safer process for the vapour phase oxidation of acetaldehyde to peroxyacetic acid has been claimed [7].

See Hydrogen peroxide: Acetic acid, or: Acetic anhydride, or: Vinyl acetate

See PEROXYACIDS (references 5,6)

See other GLASS INCIDENTS

Acetic anhydride

1. *MCA Case History No. 1795*
2. Augustine 1969, Vol. 2, 217

During an attempt to prepare an anhydrous 25% solution of peroxyacetic acid in acetic acid by dehydrating a water-containing solution with acetic anhydride, a violent explosion occurred. Mistakes in the operational procedure allowed heated evaporation to begin before the anhydride had been hydrolysed. Acetyl peroxide could have been formed from the anhydride and peroxyacid, and the latter may have detonated and/or catalysed violent hydrolysis of the anhydride [1]. A technique for preparing the anhydrous acid in dichloromethane without acetyl peroxide formation has been described [2].

See Acetic anhydride: Water

5-*p*-Chlorophenyl-2,2-dimethyl-3-hexanone

Gillespie, J. S. *et al., Tetrahedron*, 1975, **31**, 5

During the attempted preparation of 3-*p*-chlorophenylbutanoic acid by addition of the ketone (2 g mol) to peracetic acid (50%) in acetic acid at 65—70°C, a serious explosion occurred.

Ether solvents

Augustine, 1971, Vol. 2, 159

Ether solvents, such as THF, diethyl ether etc. are unsuitable solvents for peracetic acid oxidations, as interaction of the acid with the peroxidisable solvent is violent.

See other PEROXIDATION INCIDENTS

Metal chlorides

Wienhofer, E., *Chem. Ztg.*, 1980, **104**, 146

Addition of chloride ions (as solid calcium chloride, potassium chloride or sodium chloride) to aqueous solutions containing 40% of peroxyacetic acid and 1% of acetic acid leads to a violently exothermic decomposition reaction. Chlorine is evolved, most of the liquid evaporates and the residue (often red coloured) deflagrates.

See other GAS EVOLUTION INCIDENTS

3-Methyl-3-buten-1-yl tetrahydropyranyl ether

See TETRAHYDROPYRANYL ETHER DERIVATIVES

1-Octene

1. Swern, D. et al., *J. Amer. Chem. Soc.*, 1946, **68**, 1506
2. van den Brink, M. J., private comm., 1983

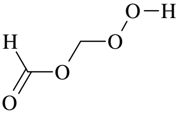
Following a published procedure [1], octene was treated with a solution of peroxyacetic acid in acetic acid for 8 h to form the epoxide, but the reaction mixture was then allowed to stand uncooled overnight. Next morning, when a 3μl sample was injected into a heated GLC injection port, the syringe shattered. This was attributed to formation of diacetyl peroxide during the overnight standing, and its subsequent explosion in the heated port [2].

Paper

See other PACKAGING INCIDENTS, PEROXYACIDS

0834. Hydroperoxymethyl formate (Formyloxymethyl hydroperoxide)

[ ] $C_2H_4O_4$



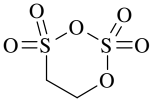
Thamm, J. *et al., Chem. Phys. Lett.*, 1996, **258**(1,2), 155

This compound was shown to be an intermediate in ozonolysis of some ethenes. In concentrated form it is very explosive; minimal handling and working with strong gloves behind a blast screen are recommended.

See other ALKYL HYDROPEROXIDES

0835. 2,4-Dithia-1,3-dioxane-2,2,4,4-tetraoxide (‘Carbyl sulfate’)

[503-41-3] $C_2H_4O_6S_2$



N-Methyl-4-nitroaniline

1. Deucker, W. *et al., Chem. Ing. Tech.*, 1973, **45**, 1040—1041
2. Wooton, D. L. *et al., J. Org. Chem.*, 1974, **39**, 2112

The title cyclic ester (1 mol) and substituted aniline (>2 mol) condense when heated in nitrobenzene solution, initially at 45°C and eventually at 75°C under vacuum in a sealed vessel, to give the ester-salt, *N*-methyl-4-nitroanilinium 2-(*N*-methyl-*N*-4-nitrophenylaminosulfonyl)ethyl sulfate. The reaction technique had been used uneventfully during 8 years, but the 3 m^3 reactor was violently ruptured when the reaction ran away and developed an internal pressure exceeding 70 bar.

Subsequent DTA investigation showed that an exothermic reaction set in above 75°C after an induction period depending on the initial temperature and concentration of reactants, which attained nearly 300°C, well above the decomposition point of the cyclic ester component (170°C). The reaction conditions used could have permitted local over-concentration and overheating effects to occur, owing to slow dissolution of the clumped solid ester and aniline in the nitrobenzene solvent [1]. Crude 'carbyl sulfate' contains excess sulfur trioxide [2].

See DIFFERENTIAL THERMAL ANALYSIS (reference 4)

See other INDUCTION PERIOD INCIDENTS, RUNAWAY REACTIONS

†0836. Thiirane (Ethylene sulfide)

[420-12-2] **C_2H_4S**

Acids

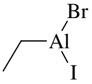
Sorbe 1968, 122

The sulfide may polymerise violently in presence of acids, especially when warm.

See related 1,2-EPOXIDES

0837. Ethylaluminium bromide iodide

[32673-60-2] **C_2H_5AlBrI**



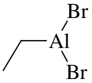
Nitromethane

See Nitromethane: Alkylmetal halides

See other ALKYLALUMINIUM HALIDES

0838. Ethylaluminium dibromide

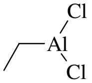
[2386-62-1] **$C_2H_5AlBr_2$**



See entry ALKYLALUMINIUM HALIDES

0839. Ethylaluminium dichloride

[563-43-9] **$C_2H_5AlCl_2$**

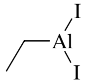


HCS 1980, 465

See entry ALKYLALUMINIUM HALIDES

0840. Ethylaluminium diiodide

[2938-73-0] **$C_2H_5AlI_2$**

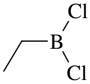


491M, 1975, 153

It ignites in air.
See other ALKYLALUMINIUM HALIDES

0841. Dichloroethylborane

[1739-53-3] **$C_2H_5BCl_2$**

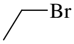


491M, 1975, 149

It ignites in air.
See other ALKYLHALOBORANES

†0842. Bromoethane (Ethyl bromide)

[74-96-4] **C_2H_5Br**

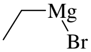


FPA H98, 1981; *HCS 1980*, 472

Preparative hazard
See Bromine: Ethanol, etc.
See other HALOALKANES

0843. Ethylmagnesium bromide

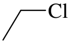
[925-90-6] **C_2H_5BrMg**



Water
Nolan, 1983, Case History 108
Ethylmagnesium bromide was prepared as usual on a large scale in one reactor, and then transferred by nitrogen pressurisation to another. The glass transfer line had not been completely dried; the ethane evolved on contact of the Grignard reagent with moisture overpressurised the line and it burst.
See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS, GRIGNARD REAGENTS

†0844. Chloroethane (Ethyl chloride)

[75-00-3] **C_2H_5Cl**



(*MCA SD-50*, 1953); *FPA H114*, 1982; *HCS 1980*, 474

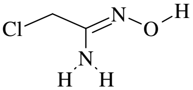
Potassium

See Potassium: Halocarbons

See other HALOALKANES

0845. 2-Chloro-*N*-hydroxyacetamidine (Chloroacetamide oxime)

[3272-96-6] **$C_2H_5ClN_2O$**



Maytum, D. M., *Chem. Brit.*, 1978, **14**, 382

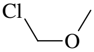
During vacuum evaporation at 60°C of ethyl acetate from a solution of the oxime, a violent explosion occurred. The oxime was found to be thermally unstable above 60°C, and at the m.p., 90°C, an exotherm of over 100°C occurred accompanied by rapid gas evolution.

See other GAS EVOLUTION INCIDENTS

See related OXIMES

†0846. Chloromethyl methyl ether

[107-30-2] **C_2H_5ClO**

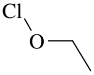


HCS 1980, 302

See related HALOALKANES

0847. Ethyl hypochlorite

[624-85-1] **C_2H_5ClO**



Alone, or Copper

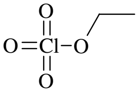
Sandmeyer, T., *Ber.*, 1885, **18**, 1768

Though distillable slowly (at 36°C), ignition or rapid heating of the vapour causes explosion, as does contact of copper powder with the cold liquid.

See other HYPOHALITES

0848. Ethyl perchlorate

[22750-93-2] **$C_2H_5ClO_4$**



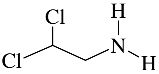
Sidgwick, 1950, 1235

Reputedly the most explosive substance known, it is very sensitive to impact, friction and heat. It is readily formed from ethanol and perchloric acid.

See other ALKYL PERCHLORATES

0849. 2,2-Dichloroethylamine

[5960-88-3] **$C_2H_5Cl_2N$**

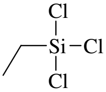


Roedig, A. *et al., Chem. Ber.*, 1966, **99**, 121

A violent explosion ocurred during evaporation of an ethereal solution at 260 mbar from a bath at 80—90°C. No explosion occurred when the bath temperature was limited to 40—45°C, or during subsequent distillation at 60—64°C/76 mbar. (Aziridine derivatives may have been formed by dehydrohalogenation.)

†0850. Trichloroethylsilane

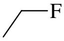
[115-21-9] **$C_2H_5Cl_3Si$**



See other ALKYLHALOSILANES

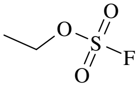
†0851. Fluoroethane (Ethyl fluoride)

[353-36-6] **C_2H_5F**



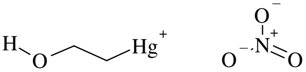
See other HALOALKANES

0852. Ethyl fluorosulfate
[371-69-7] **$C_2H_5FO_3S$**



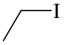
Kumar, R. C. *et al., Inorg. Chem.*, 1984, **23**, 3113—3114
The compound, prepared by by co-condensation of diethyl sulfite (3.5 mmol) and chlorine fluoride (10 mmol) at —196°C, followed by slow warming to —78, then —20°, is unstable. Trap-to-trap distillation must be effected with great care, as violent explosions occurred (even on this small scale) when cryogenic cooling was removed from the traps. Scaling up is not recommended.
See other SULFUR ESTERS

0853. 2-Hydroxyethylmercury(II) nitrate
[51821-32-0] **$C_2H_5HgNO_4$**



Whitmore, 1921, 110
It decomposes with a slight explosion on heating.
See other MERCURY COMPOUNDS, ORGANOMETALLIC NITRATES

0854. Iodoethane (Ethyl iodide)
[75-03-6] **C_2H_5I**

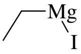


HCS 1980, 561

Preparative hazard
See Iodine: Ethanol, etc.

Silver chlorite
See Silver chlorite: Iodoalkanes
See other HALOALKANES

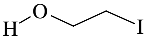
0855. Ethylmagnesium iodide
[10467-10-4] **C_2H_5IMg**



Ethoxyacetylene
Jordan, C. F., *Chem. Eng. News*, 1966, **44**(8), 40

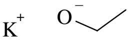
A stirred mixture of ethoxyacetylene with ethylmagnesium iodide in ether exploded when the agitator was turned off. The corresponding bromide had been used without incident in earlier smaller-scale attempts.
See other AGITATION INCIDENTS, ALKYLMETAL HALIDES, GRIGNARD REAGENTS

0856. 2-Iodoethanol
[624-76-0] **C_2H_5IO**



Trimethylstibine
See 2-Hydroxyethyltrimethylstibonium iodide
See related HALOALKANES

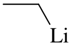
0857. Potassium ethoxide
[917-58-8] **C_2H_5KO**



1. *See entry* METAL ALKOXIDES
2. Anon. private comm., 1984

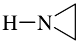
It may ignite in moist air [1]. The dry powder is very dusty, and suspensions in dry air have a low minimum ignition energy, 17.1 mJ. After an induction period depending on the temperature and humidity of the atmosphere, a sample confined in a Dewar flask decomposed rapidly, with an exotherm of 200°C. Heats of solution in ethanol and in water are 0.63 and 0.65 kJ/g, respectively [2].
See other INDUCTION PERIOD INCIDENTS

0858. Ethyllithium
[811-49-4] **C_2H_5Li**



Sorbe, 1968, 82
It ignites in air.
See other ALKYLMETALS

†0859. Aziridine (Ethylenimine)
[151-56-4] **C_2H_5N**



HCS 1980, 169

Significantly endothermic; ΔH_f° 92 kJ/mole, 2.4 kJ/g
See other ENDOTHERMIC COMPOUNDS

Acids
'Ethylenimine', Brochure 125-521-65, Midland (Mich.), Dow Chemical Co., 1965

It is very reactive chemically and subject to aqueous auto-catalysed exothermic polymerisation, which may be violent if uncontrolled by dilution, slow addition or cooling. It is normally stored over solid caustic alkali, to minimise polymerisation catalysed by presence of carbon dioxide.
See other CATALYTIC IMPURITY INCIDENTS, POLYMERISATION INCIDENTS

Aluminium chloride, Substituted anilines
Lehman, D. *et al., Chem. Abs.*, 1983, **98**, 125559
In the preparation of a series of substituted phenylethylenediamines, it is essential to add the reagents to an aromatic solvent at 30—80°C in the order aniline, then aluminium chloride, then ethylenimine to prevent uncontrollable exothermic reaction.

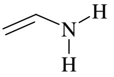
Chlorinating agents
Graefe, A. F. *et al., J. Amer. Chem. Soc.*, 1958, **80**, 3939
It gives the explosive 1-chloroaziridine on treatment with, e.g. sodium hypochlorite solution.
See 1-Chloroaziridine

Dinitrogen pentaoxide
See Dinitrogen pentaoxide: Strained ring heterocycles

Preparative hazard
Energy of decomposition (in range 130—390°C) measured as 2.02 kJ/g.
See 2-Chloroethylammonium chloride: Alkali
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

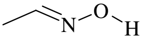
Silver
'Ethylenimine' Brochure 125-521-65, Midland (Mich.), Dow Chemical Co., 1965
Explosive silver derivatives may be formed in contact with silver or its alloys, including silver solder, which is therefore unsuitable in handling equipment.
See other AZIRIDINES

0860. Vinylamine (Etheneamine)
[593-67-9] **C_2H_5N**



Isoprene
Seher, A., *Ann.*, 1952, **575**, 153—161
Attempts at interaction led to explosions.

†0861. Acetaldehyde oxime (Hydroximinoethane)
[107-29-9] **C_2H_5NO**

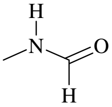


HCS 1980, 98

See other OXIMES

0862. *N*-Methylformamide

[123-39-7] **C_2H_5NO**

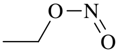


HCS 1980, 670

See other APROTIC SOLVENTS

†0863. Ethyl nitrite

[109-95-5] **$C_2H_5NO_2$**

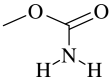


Haz. Chem. Data, 1975, 161

It may decompose explosively around 90°C.
See other ALKYL NITRITES

0864. Methyl carbamate

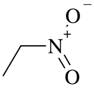
[598-55-0] **$C_2H_5NO_2$**



Phosphorus pentachloride
See N-Carbomethoxyiminophosphoryl chloride

0865. Nitroethane

[79-24-3] **$C_2H_5NO_2$**



HCS 1980, 682

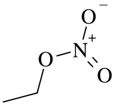
1. Kirk-Othmer, 1996, Vol. 17, 216
2. *Beilsteins Handbuch der organischen Chemie*, **H**(1), 101, Springer, Berlin, 1918

Although it is certainly less explosive, being detonable only if both hot and heavily confined [1], many reference works recommend precautions similar to those for nitromethane. The sodium salt explodes on heating [2].
See Nitromethane

Metal oxides
See other NITROALKANES: METAL OXIDES

Other reactants
Yoshida, 1980, 271
MRH values calculated for 13 combinations with oxidants are given.
See other NITROALKANES

†0866. Ethyl nitrate
[625-58-1] **$C_2H_5NO_3$**

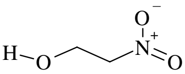


Hydrocarbons, Oxygen
See Oxygen: Hydrocarbons, Promoters

Lewis acids
See other ALKYL NITRATES (references 2,3)

Other reactants
Yoshida, 1980, 191
MRH values calculated for 7 combinations are given.
See other ALKYL NITRATES

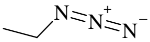
0867. 2-Nitroethanol
[625-48-9] **$C_2H_5NO_3$**



1. Anon., *ABCM Quart. Safety Summ.*, 1956, **27**, 24
2. Noland, W. E., *Org. Synth. Coll. Vol. 5*, 1973, 836

An explosion occurred towards the end of vacuum distillation of a relatively small quantity of 2-nitroethanol. This was attributed to the presence of peroxides, but the presence of traces of alkali seems a possible alternative cause [1]. Explosion of distillation residues, especially on exposure to air, is likely in the absence of a chaser and diluent, diphenyl ether is suggested in the latter role [2].
See other C-NITRO COMPOUNDS

0868. Ethyl azide
[871-31-8] **$C_2H_5N_3$**



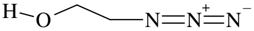
1. Boyer, J. H. *et al., Chem. Rev.*, 1954, **54**, 32
2. Koch, E., *Angew. Chem. (Nachr.)*, 1970, **18**, 26
3. Burns, M. E. *et al., Chem. Eng. News*, 1985, **63**(50), 2
4. Nielsen, C. J. *et al., Spectrochim. Acta A*, 1988, **44A**, 409—422

Though stable at room temperature, it may detonate on rapid heating [1]. A sample stored at —55°C exploded after a few minutes' exposure at ambient temperature, possibly owing to development of internal pressure in the stoppered vessel. It will also explode if dropped from 1 m in a small flask on to a stone floor [2]. An explosion occurred during laboratory preparation of ethyl azide when bromomethyl blue indicator was added to the reaction mixture to show the pH. This was attributed either to the acidic nature of the indicator, or to exposure of the azide vapour to the ground glass joint. Precautions recommended are similar to those when using diazomethane, and include small scale working, no ground joints, protection from intense light, and dilution of the product with solvent [3]. A safe synthesis is described, and IR, NMR and Raman spectral data were recorded in vapour, liquid and solid states [4].

See other GLASS INCIDENTS, ORGANIC AZIDES

0869. 2-Azidoethanol

[1517-05-1] **$C_2H_5N_3O$**



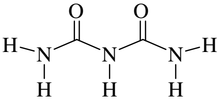
1. Appleby, I. C., *Chem. & Ind.*, 1986, 337
2. Appleby, I. C., private comm., 1987

During the preparation of 2-azidoethanol from a stirred mixture of 2-bromoethanol (14.6 mol) and sodium azide (15.4 mol) heated on a steam bath, a violent explosion occurred after 100 min. The preparation had been carried out previously without mishap. The need for care in handling azides of low MW is stressed [1]. Later detailed studies showed that the most probable cause of the explosion was the extraordinarily high mechanical and thermal sensitivity of the compound, with initiation by vibration from the agitator [2].

See other ORGANIC AZIDES

0870. Imidodicarbonic diamide (Biuret)

[108-19-0] **$C_2H_5N_3O_2$**

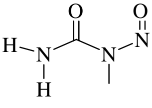


Chlorine

See Chlorine: Nitrogen compounds

0871. *N*-Methyl-*N*-nitrosourea

[684-93-5] **$C_2H_5N_3O_2$**



1. Arndt, F., *Org. Synth.*, 1943, Coll. Vol. 2, 462
2. Anon., *Angew. Chem. (Nachr.)*, 1957, **5**, 198
3. Anon., *Jahresber.*, 1978, 70—71
4. *See entry* SELF-ACCELERATING REACTIONS

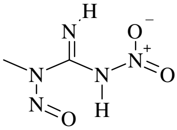
This must be stored under refrigeration to avoid sudden decomposition after storage at ambient temperature or slightly above (30°C) [1]. More stable precursors for generation of diazomethane are now available. Material stored at 20°C exploded after 6 months [2]. Explosive decomposition and ignition of solvent ether occured when 50 g of the compound in a nickel spoon was being added to 40% potassium hydroxide solution to generate diazomethane [3]. DSC examination of several *N*-nitroso compounds showed that most underwent self accelerating decomposition, some with extraordinary velocity. The time to maximum rate for the urea falls from 1200 min at 40° to near zero at 80°C, when the maximum heat flow is 8.7 J/s/g [4].

See Diazomethane

See other NITROSO COMPOUNDS

0872. 1-Methyl-3-nitro-1-nitrosoguanidine

[70-25-7] **$C_2H_5N_5O_3$**



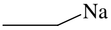
1. Eisendrath, J. N., *Chem. Eng. News*, 1953, **31**, 3016
2. Aldrich advertisement, *J. Org. Chem.*, 1974, **39**(7), cover iv

Formerly used as a diazomethane precursor, this material will detonate under high impact, and a sample exploded when melted in a sealed capillary tube [1]. Although the crude product from the aqueous nitrosation is pyrophoric, recrystallised material is stable (though powerfully mutagenic) [2].

See other N—NITRO COMPOUNDS, NITROSO COMPOUNDS

0873. Ethylsodium

[676-54-0] **C_2H_5Na**



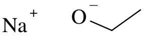
Houben-Weyl, 1970, Vol. 13.1, 384

The powder ignites in air.

See other ALKYLMETALS

0874. Sodium ethoxide

[141-52-6] **C_2H_5NaO**

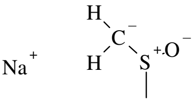


May ignite in moist air.

See entry METAL ALKOXIDES

0875. Sodium dimethylsulfinate

[58430-57-2] **C_2H_5NaOS**



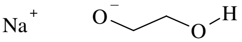
4-Chlorotrifluoromethylbenzene

See 4-Chlorotrifluoromethylbenzene: Sodium dimethylsulfinate

See Dimethyl sulfoxide: Sodium hydride

0876. Sodium 2-hydroxyethoxide

[7388-28-5] **$C_2H_5NaO_2$**



Polychlorobenzenes

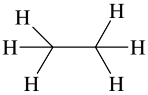
Milnes, M. H., *Nature*, 1971, **232**, 395—396

It was found that the monosodium salt of ethylene glycol decomposed at about 230°C, during an investigation of the 1968 Coalite explosion during the preparation of 2,3,5-trichlorophenol by hydrolysis of 1,2,4,5-tetrachlorobenzene with sodium hydroxide in ethylene glycol at 180°C. Decomposition in the presence of polychlorobenzenes was exothermic and proceeded rapidly and uncontrollably, raising the temperature to 410°C, and liberating large volumes of white vapours, one of which was identified as ethylene oxide. The decomposition proceeded identically in presence of the tetrachlorobenzene or the 3 isomeric trichlorobenzenes (and seems also likely to occur in the absence of these or the chlorophenols produced by hydrolysis). The latter view has now been confirmed.

See Sodium hydroxide: Glycols

†0877. Ethane

[74-84-0] **C_2H_6**

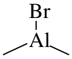


FPA H37, 1975; *HCS 1980*, 456 (cylinder)

Chlorine
See Chlorine: Hydrocarbons

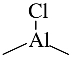
Dioxygenyl tetrafluoroborate
See Dioxygenyl tetrafluoroborate: Organic materials

0878. Dimethylaluminium bromide
[3017-85-4] **C_2H_6AlBr**



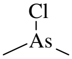
Nitromethane
See Nitromethane: Alkylmetal halides
See other ALKYLALUMINIUM HALIDES

0879. Dimethylaluminium chloride
[1184-58-3] **C_2H_6AlCl**



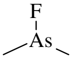
Air, or Water
Gaines, D. F. *et al., Inorg. Chem.*, 1974, **15**, 203—204
It ignites in air and reacts violently with water.
See other ALKYLALUMINIUM HALIDES

0880. Chlorodimethylarsine
[557-89-1] **C_2H_6AsCl**



Leleu, *Cahiers*, 1977, (88), 362
It ignites in air, even at 0°C.
See other ALKYLNON-METAL HALIDES

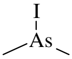
0881. Dimethylfluoroarsine
[420-23-5] **C_2H_6AsF**



Leleu, *Cahiers*, 1977, (88), 363
It ignites in air.
See other ALKYLNON-METAL HALIDES

0882. Dimethyliodoarsine

[676-75-5] **C_2H_6AsI**



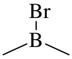
Millar, I. T. *et al., Inorg. Synth.*, 1960, **6**, 117

It ignites when heated in air.

See other ALKYLNON-METAL HALIDES

0883. Bromodimethylborane

[5158-50-9] **C_2H_6BBr**



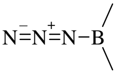
Katz, H. E., *J. Org. Chem.*, 1985, 50, **50**28

It is pyrophoric in air.

See other ALKYLHALOBORANES, PYROPHORIC MATERIALS

0884. Azidodimethylborane

[7360-67-0] **$C_2H_6BN_3$**



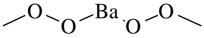
Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 27

A sample exploded on contact with a warm sampling capillary.

See other NON-METAL AZIDES

0885. Barium methyl hydroperoxide

[ ] **$C_2H_6BaO_4$**

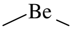


See Methyl hydroperoxide

See related ALKYL HYDROPEROXIDES

0886. Dimethylberyllium

[506-63-8] **C_2H_6Be**



Air, or Carbon dioxide, or Water

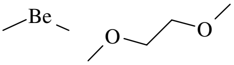
Coates, 1967, Vol. 1, 106

It ignites in moist air or in carbon dioxide, and reacts explosively with water.

See other ALKYLMETALS

0887. Dimethylberyllium—1,2-dimethoxyethane

[ ] **$C_2H_6Be.C_4H_{10}O_2$**



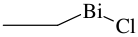
Houben-Weyl, 1973, Vol. 13.2a, 38

It ignites in air.

See related ALKYLMETALS

0888. Chloroethylbismuthine

[65313-33-9] **C_2H_6BiCl**



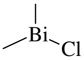
Leleu, *Cahiers*, 1977, (88), 364

It ignites in air.

See related ALKYLMETAL HALIDES, ALKYLMETAL HYDRIDES

0889. Dimethylbismuth chloride

[ ] **C_2H_6BiCl**



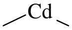
Sidgwick, 1950, 781

It ignites when warm in air.

See other ALKYLMETAL HALIDES

0890. Dimethylcadmium

[506-82-1] **C_2H_6Cd**



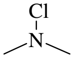
1. Egerton, A. *et al., Proc. R. Soc.*, 1954, **A225**, 429
2. Davies, A.G., *Chem. & Ind.*, 1958, 1177
3. Sidgwick, 1950, 268

On exposure to air, dimethylcadmium peroxide is formed as a crust [1] which explodes on friction [2]. Ignition of dimethylcadmium may occur if a large area: volume ratio is involved, as when it is dripped onto filter paper [3]. It is a mildly endothermic compound (ΔH_f° (l) +67.8 kJ/mol, 0.47 kJ/g).

See other ALKYLMETALS, ENDOTHERMIC COMPOUNDS

0891. *N*-Chlorodimethylamine

[1585-74-6] **C_2H_6ClN**



Antimony chlorides

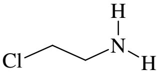
Weiss, W. *et al., Z. Anorg. Chem.*, 1977, **433**, 207—210

The crystalline addition compounds formed with antimony trichloride and antimony pentachloride in dichloromethane at —78°C tend to explode at ambient temperature, or when shocked or heated.

See other N-HALOGEN COMPOUNDS

0892. 2-Chloroethylamine

[689-98-5] **C_2H_6ClN**



It may polymerise explosively.

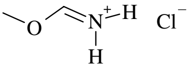
See 2-Chloroethylammonium chloride: Alkali

See also 2-Chloro-1,4-phenylenediamine

See other POLYMERISATION INCIDENTS

0893. Methyl iminioformate chloride

[15755-09-6] **C_2H_6ClNO**

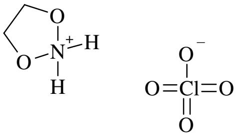


Preparative hazard

See Hydrogen chloride: Alcohols, Hydrogen cyanide

0894. 2-Aza-1,3-dioxolanium perchlorate (Ethylenedioxyammonium perchlorate)

[ ] **$C_2H_6ClNO_6$**

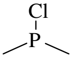


MCA Case History No. 1622

A batch of this sensitive compound (low oxygen balance) exploded violently, probably during recrystallisation.

See other N—O COMPOUNDS, PERCHLORATE SALTS OF NITROGENOUS BASES

0895. Chlorodimethylphosphine
[811-62-1] **C_2H_6ClP**

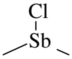


1. Staendeke, H. *et al., Angew. Chem. (Intern. Ed.)*, 1973, **12**, 877
2. Parshall, G. W., *Inorg. Synth.*, 1974, **15**, 192—193

It ignites in contact with air [1], and handling procedures are detailed [2].

See other ALKYLHALOPHOSPHINES

0896. Dimethylantimony chloride
[18380-68-2] **C_2H_6ClSb**

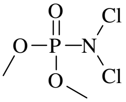


Sidgwick, 1950, 777

It ignites at 40°C in air.

See other ALKYLMETAL HALIDES

0897. Dimethyl *N,N*-dichlorophosphoramidate
[29727-86-4] **$C_2H_6Cl_2NO_3P$**

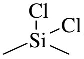


Preparative hazard

See Chlorine: Dimethyl phosphoramidate

See other *N*-HALOGEN COMPOUNDS, PHOSPHORUS ESTERS

†0898. Dichlorodimethylsilane
[75-78-5] **$C_2H_6Cl_2Si$**



HCS 1980, 428

Water

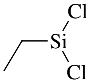
Leleu, *Cahiers*, 1977, (88), 370

Violent reaction with water.

See other ALKYLHALOSILANES

†0899. Dichloroethylsilane

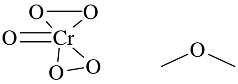
[1789-58-8] **$C_2H_6Cl_2Si$**



See other ALKYLHALOSILANES

0900. (Dimethyl ether)oxodiperoxochromium(VI)

[ ] **$C_2H_6CrO_6$**



Schwarz, R. *et al., Ber.*, 1936, **69**, 575

The blue solid explodes powerfully at —30°C.

See related AMMINECHROMIUM PEROXOCOMPLEXES

0901. Copper(II) glycinate nitrate (Aquaglycinatonitratocopper)

[94791-14-7] **$C_2H_6CuN_2O_6$**

$H_2NCH_2CO.OCuONO_2.H_2O$

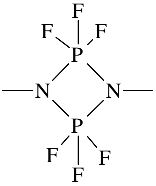
Davies, H. O. *et al., J. Chem. Soc. Chem. Comm.*, 1992, (3), 226

The mixed salt explodes on heating to 167°C, first losing water.

See related METAL NITRATES

0902. 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine

[3880-04-4] **$C_2H_6F_6N_2P_2$**

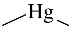


tert-Butyllithium

See tert-Butyllithium: 2,2,2,4,4,4-Hexafluoro-1,3,2,4-diazadiphosphetidine

0903. Dimethylmercury

[593-74-8] **C_2H_6Hg**



It is mildly endothermic (ΔH_f° (l) +75.3 kJ/mol, 0.33 kJ/g).

Diboron tetrachloride

See Diboron tetrachloride: Dimethylmercury

See other ALKYLMETALS, ENDOTHERMIC COMPOUNDS, MERCURY COMPOUNDS

0904. Dimethylmagnesium

[2999-74-8] **C_2H_6Mg**

Air, or Water

Gilman, H. *et al., J. Amer. Chem. Soc.*, 1930, **52**, 5049

Contact with moist air usually caused ignition of the dry powder, and water always ignited the solid or its ethereal solution.

See other ALKYLMETALS, DIALKYLMAGNESIUMS

0905. Dimethylmanganese

[33212-68-9] **C_2H_6Mn**

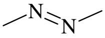
1. Bailar, 1973, Vol. 3, 851; Vol. 4, 792
2. *491M 1975*, 159

It is a readily explosive powder, (probably polymeric) [1], which also ignites in air [2].

See other ALKYLMETALS

0906. Azomethane (Dimethyldiazene)

[503-28-6] **$C_2H_6N_2$**



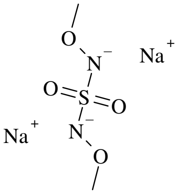
Allen, A. O. *et al., J. Amer. Chem. Soc.*, 1935, **57**, 310—317

The slow thermal decomposition of gaseous azomethane becomes explosive above 341°C/250 mbar and 386°C/24 mbar.

See other AZO COMPOUNDS

0907. Disodium *N,N′*-dimethoxysulfonyldiamide

[ ] **$C_2H_6N_2Na_2O_4S$**



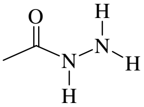
Goehring, 1957, 87

The dry solid readily explodes, as do many *N*-metal hydroxylamides.

See other *N*-METAL DERIVATIVES, N—O COMPOUNDS

0908. Acetohydrazide

[1068-57-1] **$C_2H_6N_2O$**

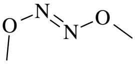


Energy of decomposition (in range 460—510°C) measured as 1.02 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

0909. Dimethyl hyponitrite (Dimethoxydiazene)

[29128-41-4] **$C_2H_6N_2O_2$**



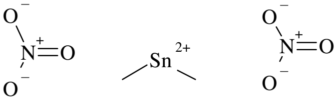
Mendenhall, G. D. *et al., J. Org. Chem.*, 1975, **40**, 1646

Samples of the ester exploded violently during low-temperature distillation, and on freezing by liquid nitrogen. The undiluted liquid is exceptionally unpredictable, but addition of mineral oil before vaporisation improved safety aspects.

See other DIALKYL HYPONITRITES

0910. Dimethyltin dinitrate

[40237-34-1] **$C_2H_6N_2O_6Sn$**



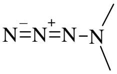
Sorbe, 1968, 159

It decomposes explosively on heating.

See other ORGANOMETALLIC NITRATES

0911. *N*-Azidodimethylamine

[2156-66-3] **$C_2H_6N_4$**

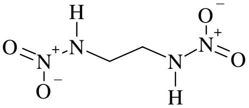


Bock, H. *et al., Angew. Chem.*, 1962, **74**, 327

It is rather explosive.

See related ORGANIC AZIDES

0912. *N,N′*-Dinitro-1,2-diaminoethane
[505-71-5] **$C_2H_6N_4O_4$**



1. Urbanski, 1967, Vol. 3, 20
2. Stull, 1977, 20

This powerful but relatively insensitive explosive decomposes violently at 202°C, and gives lead and silver salts which are highly impact sensitive [1]. Though not endothermic (ΔH_f° —103.3 kJ/mol), as a bis-nitramine it has a rather high heat of decomposition (3.91 kJ/g) which it is calculated would attain an adiabatic decomposition temperature over 2250°C, with a 60-fold pressure increase in a closed system [2].

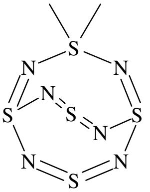
See other N—NITRO COMPOUNDS

Amminemetals

Complexes with several ammine derivatives of metals are explosive.

See entry NITRAMINE—METAL COMPLEXES

0913. *S,S*-Dimethylpentasulfur hexanitride
[71901-54-7] **$C_2H_6N_6S_5$**

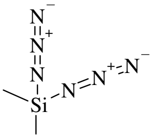


Sheldrick, W. S. *et al., Inorg., Chem.*, 1980, **19**, 339

Powerfully explosive like the non-methylated compound, breaking the quartz combustion tubes during microanalysis.

See other N—S COMPOUNDS

0914. Diazidodimethylsilane
[4774-73-6] **$C_2H_6N_6Si$**



Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 26—27

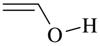
A 3 year old sample exploded violently on removing the ground stopper.

See other FRICTIONAL INITIATION INCIDENTS, NON-METAL AZIDES

†0915. Dimethyl ether (Oxybismethane)
[115-10-6] **C_2H_6O**

FPA H113, 1983, *HCS 1980*, 429

†0916. Ethanol (Ethyl alcohol)
[64-17-5] **C_2H_6O**



NSC 391, 1968; *FPA H2*, 1972; *HCS 1980*, 639; *RSC Lab. Hazard Data Sheet No. 50*, 1986

Acetic anhydride, Sodium hydrogensulfate
See Acetic anhydride: Ethanol, etc.

Acetyl bromide
See Acetyl bromide: Hydroxylic compounds

Ammonia, Silver nitrate
See Silver nitrate: Ammonia, Ethanol

Dichloromethane, Sulfuric acid, (A nitrate or nitrite?)
See Sulfuric acid, Dichloromethane, etc.

Disulfuric acid, Nitric acid
See Nitric acid: Alcohols, Disulfuric acid

Disulfuryl difluoride
See Disulfuryl difluoride: Ethanol

Magnesium perchlorate
See Magnesium perchlorate: Ethanol

Nitric acid, Silver
See Silver: Ethanol, Nitric acid

Other reactants
Yoshida, 1980, 43
MRH values calculated for 18 combinations with oxidants are given.

Oxidants MRH values show % of oxidant
See Barium perchlorate: Alcohols
Bromine pentafluoride: Hydrogen-containing materials
Calcium hypochlorite: Hydroxy compounds MRH 2.30/93
Chloryl perchlorate: Organic matter
Chromium trioxide: Alcohols MRH 2.55/90
Chromyl chloride: Organic solvents

Dioxygen difluoride: Various materials
'Fluorine nitrate': Organic materials
Hydrogen peroxide: Alcohols MRH 6.19/21
Iodine heptafluoride: Organic solvents
Nitric acid: Alcohols MRH 5.56/76
Nitrosyl perchlorate: Organic materials
Perchloric acid: Alcohols MRH 6.28/79
Permanganic acid: Organic materials
Peroxodisulfuric acid: Organic liquids
Potassium dioxide: Ethanol
Potassium perchlorate: Ethanol
Potassium permanganate: Ethanol, etc. MRH 2.68/91
Ruthenium(VIII) oxide: Organic materials
Silver perchlorate: Aromatic compounds MRH 3.30/87
Sodium peroxide: Hydroxy compounds MRH 2.43/91
Uranium hexafluoride: Aromatic hydrocarbons, etc.
Uranyl perchlorate: Ethanol

See *N*-HALOMIDES: ALCOHOLS

Phosphorus(III) oxide
See Tetraphosphorus hexaoxide: Organic liquids

Platinum
See Platinum: Ethanol

Potassium
See Potassium: Slow oxidation

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

Silver nitrate
See Silver nitrate: Ethanol

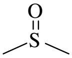
Silver oxide
See Silver(I) oxide: Ammonia, etc.

Sodium
See Sodium: Ethanol

Tetrachlorosilane
See Tetrachlorosilane: Ethanol

†0917. Dimethyl sulfoxide (Sulfinylbismethane)

[67-68-5] **C_2H_6OS**



HCS 1980, 435; *RSC Lab. Hazard Data Sheet No. 11*, 1983

1. Brogli, F. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 681—682, Basle, SSCI, 1980
2. Cardillo, P. *et al., Chim. e Ind.* (Milan), 1982, **44**, 231—234
3. Santosusso, T. M. *et al., Tetrahedron Lett.*, 1974, 4255—4258
4. *See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Two instances of used DMSO decomposing exothermally while being kept at 150°C prior to recovery by vacuum distillation were investigated. Traces of alkyl bromides lead to a delayed, vigorous and strongly exothermic reaction ($Q = 0.85$ kJ/g) at 180°C. Addition of zinc oxide as a stabiliser extends the induction period and markedly reduces the exothermicity [1]. ARC examination shows that exothermic decomposition sets in by a radical mechanism at 190°C, just above the b.p., 189°C. The proposed retardants, sodium carbonate and zinc oxide, do not affect the decomposition temperature, and a maximum decomposition pressure of 60 bar was attained (at up to 4 bar/min) at the low sample loading of 18 w/v% in the bomb [2]. The thermolytic degradation of the sulfoxide to give acidic products which catalyse further decomposition had been discussed previously [3]. T_{ait24} was determined as 213°C by adiabatic Dewar tests, with an apparent energy of activation of 243kJ/mol. At elevated temperatures (200°C) DSC shows decomposition to be both faster and more energetic when chloroform or sodium hydroxide is present.

See other INDUCTION PERIOD INCIDENTS, SELF-ACCELERATING REACTIONS

Acid anhydrides

See Trifluoroacetic anhydride, below

Acids, or Bases

Hall, J., *Loss Prev. Bull.*, 1993, (114), 2

These may catalyse exothermic decomposition. A runaway of a mixture with 4-nitrobenzenesulfonic acid, possibly from as low as 60°C (though a steam valve may have been leaking) is reported by Hall.

See reference 2, next below

Acyl halides, or Non-metal halides MRH Thionyl chloride 1.63/60

1. Buckley, A., *J. Chem. Educ.*, 1965, **42**, 674
2. Allan, G. G. *et al., Chem. & Ind.*, 1967, 1706
3. Mancuso, A. J. *et al., J. Org. Chem.*, 1979, **44**, 4148—4150

In absence of diluent or other effective control of reaction rate, the sulfoxide reacts violently or explosively with the following: acetyl chloride, benzenesulfonyl chloride, cyanuric chloride, phosphorus trichloride, phosphoryl chloride, tetrachlorosilane, sulfur dichloride, disulfur dichloride, sulfuryl chloride or thionyl chloride [1]. These violent reactions are explained in terms of exothermic polymerisation of formaldehyde produced under a variety of conditions by interaction of the sulfoxide with reactive halides, acidic or basic reagents [2]. Oxalyl chloride reacts explosively with DMSO at ambient temperature, but controllably in dichloromethane at —60°C [3].

See Carbonyl diisothiocyanate, and Dinitrogen tetraoxide, and Hexachlorocyclotriphosphazine, and Sodium hydride, all below

See Perchloric acid: Sulfoxides

Allyl trifluoromethanesufonates

See ALLYL TRIFLUOROMETHANESULFONATES: ALONE, OR APROTIC SOLVENTS

Boron compounds

Shriver, 1969, 209

DMSO forms an explosive mixture with nonahydrononaborate(2—) ion and with diborane. It is probable that other boron hydrides and hydroborates behave similarly.

Bromides

1. Hall, J., *Loss Prev. Bull.*, 1993, (114), 2
2. Aida, T., *et al., Bull. Chem. Soc. Jap.*, 1976, **49**, 117

A review of runaway decomposition reactions of DMSO [1], several involving bromides, some alkaline and under vacuum, from temperatures possibly as low as 130°C. A bromide/bromine catalysed decomposition reaction is known [2].

4(4'-Bromobenzoyl)acetanilide

491M, 1975, 74

An explosion occurred after a solution of the anilide in DMSO had been held at 100°C for 30 min.

Bromomethane

See Trimethylsulfoxonium bromide

Carbonyl diisothiocyanate

Bunnenberg, R. *et al., Chem. Ber.*, 1981, **114**, 2075—2086

Interaction of the solvent with the strong electrophile is explosive.

See Acyl halides, above

Copper, Trichloroacetic acid

1. Giessemann, B. W., *Chem. Eng. News*, 1981, **59**(28), 4
2. Dunne, T. G. *et al., Chem. Eng. News*, 1981, **59**(50), 4

The acid was added to copper wool and rinsed down with DMSO. Within 20 s, the contents of the flask were ejected and the neck was distorted by intense heat [1]. Adding the copper wool to a solution of the acid in the solvent gave an exothermic but controlled reaction [2]. (Formation of a reactive carbene species by dehydrohalogenation seems a remote possibility.)

See Acyl halides, above

Dichloromethane, Perchloric acid

See Perchloric acid: Dichloromethane, Dimethyl sulfoxide

Dinitrogen tetraoxide

Buckley, A., *J. Chem. Educ.*, 1965, **42**, 674

Interaction may be violent or explosive.

See Acyl halides

See Nitric acid: Dimethyl sulfoxide

Hexachlorocyclotriphosphazine

Pierce, T. *et al., Lab. Haz. Bull.*, 1984, (4), item 215

Addition of about 100 mg of hexachlorocyclotriphosphazine (also containing some phenoxylated products) to 0.5 ml of DMSO in an NMR tube led to an exothermic reaction which ejected the tube contents. General precautions are suggested.
See Acyl halides, above

Iodine pentafluoride
Lawless, E. M., *Chem. Eng. News*, 1969, **47**(13), 8
Interaction is explosive, after a delay, in either tetrahydrothiophene-1,1-dioxide (sulfolane) or trichlorofluoromethane as solvent, on 0.15 g mol scale, though not on one tenth this scale.

Magnesium perchlorate MRH 5.52/78
See Magnesium perchlorate: Dimethyl sulfoxide

Metal alkoxides
MCA Case History No. 1718
Addition of potassium *tert*-butoxide or of sodium isopropoxide to the solvent led to ignition of the latter. This was attributed to presence of free metal in the alkoxides, but a more likely explanation seems to be that of direct interaction between the powerful bases and the sulfoxide.
Potassium *tert*-butoxide: Acids, etc.
See Acids, or Bases, above (reference 2)

Metal oxosalts

1. Martin, 1971, 435
2. Dehn, H., Brit. Pat. 1 129 777, 1968
3. Sandstrom, M. *et al., Acta Chem. Scand.*, 1978, **A32**, 610

Mixtures of the sulfoxide with metal salts of oxoacids are powerful explosives. Examples are aluminium perchlorate, sodium perchlorate and iron(III) nitrate [1]. The water in hydrated oxosalts (aluminium perchlorate, iron(III) perchlorate, iron(III) nitrate) may be partially or totally replaced by dimethyl (or other) sulfoxide to give solvated salts useful as explosives [2]. Metal nitrates and perchlorates solvated with DMSO are generally powerfully explosive, and under certain conditions a violent reaction is easily triggered [3]. Several other explosions involving perchlorates and the sulfoxide have been reported.
See Perchloric acid: Sulfoxides
Magnesium perchlorate: Dimethyl sulfoxide
Mercury(II) perchlorate . 6(or 4)dimethyl sulfoxide
Silver perchlorate: Dimethyl sulfoxide
See Chromium(III) perchlorate . 6dimethyl sulfoxide

Nitric acid
See Nitric acid: Dimethyl sulfoxide

Non-metal halides
See Acyl halides, etc., above

Other reactants
Yoshida, 1980, 171
MRH values calculated for 6 combinations are given.

Perchloric acid MRH 6.19/77

See Perchloric acid: Sulfoxides

Periodic acid

See Periodic acid: Dimethyl sulfoxide

Phosphorus(III) oxide

See Tetraphosphorus hexaoxide: Organic liquids

Potassium

Houben-Weyl 1970, Vol. 13.1, 295

Interaction of potassium 'sand' and dimethyl sulfoxide is violent in the absence of a diluent, and leads to partial decomposition of the potassium dimethylsulfinate. THF is a suitable diluent.

See Metal alkoxides, above

Potassium permanganate MRH 3.01/14

See Potassium permanganate: Dimethyl sulfoxide

Silver difluoride

Lawless, E. M., *Chem. Eng. News*, 1969, **47**(13), 8

Interaction is violent.

Sodium

Hall, J., *Loss Prev. Bull.*, 1993, (114), 2

A preparation of dimsyl sodium from sodium and DMSO, on 14 litre scale, overheated, then exploded causing two fatalities. It has not proved possible to duplicate the runaway.

Sodium hydride

1. French, F. A., *Chem. Eng. News*, 1966, **44**(15), 48
2. Olson, G. A., *Chem. Eng. News*, 1966, **44**(24), 7
3. Russell, G. A. *et al., J. Org. Chem.*, 1966, **31**, 248
4. Batchelor, J. F., private comm., 1976
5. Anon., *Loss Prev. Bull.*, 1980, (030), 161
6. Allan, G. G. *et al., Chem. & Ind.*, 1967, 1706
7. Itoh, M. *et al., Lab. Haz. Bull.* 1985(5), item 304

Two violent pressure-explosions occurred during preparations of dimethylsulfinyl anion on 3—4 g mol scale by reaction of sodium hydride with excess solvent. In each case, the explosion occurred soon after separation of a solid. The first reaction involved addition of 4.5 g mol of hydride to 18.4 g mol of sulfoxide, heated to 70°C [1], and the second 3.27 and 19.5 g mol respectively, heated to 50°C [2]. A smaller scale reaction at the original lower hydride concentration [3], did not explode, but methylation was incomplete. Explosions and fire occurred when the reaction mixture was overheated (above 70°C) [4]. Reaction of 1 g mol of hydride with 0.5 l of sulfoxide at 80°C led to an exotherm to 90°C with explosive decomposition [5]. These and similar incidents are explicable in terms of exothermic polymerisation of formaldehyde produced from sulfoxide by reaction with the hydride base [6]. The heat of reaction was calculated and determined experimentally. Thermal decomposition of the solution of hydride is not very violent, but begins at low temperatures, with gas evolution [7].

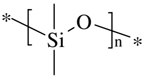
See Sodium dimethylsulfinate
See other GAS EVOLUTION INCIDENTS

Sulfur trioxide MRH 2.51/59
See Sulfur trioxide: Dimethyl sulfoxide

Trifluoroacetic anhydride
Sharma, A. K. *et al., Tetrahedron Lett.*, 1974, 1503—1506
Interaction of the sulfoxide with some acid anhydrides or halides may be explosive. The highly exothermic reaction with trifluoroacetic anhydride was adequately controlled in dichloromethane solution at below —40°C.
See Acyl halides, above
See other APROTIC SOLVENTS

0918. Poly(dimethylsiloxane)

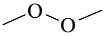
[9016-00-6] **$(C_2H_6OSi)_n$**



See SILICONE OIL

0919. Dimethyl peroxide

[690-02-8] **$C_2H_6O_2$**

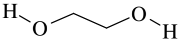


1. Rieche, A. *et al., Ber.*, 1928, **61**, 951
2. Baker, G. *et al., Chem. & Ind.*, 1964, 1988

Extremely explosive, heat- and shock-sensitive as liquid or vapour [1]. During determination of the impact-sensitivity of the confined material, rough handling of the container caused ignition. The material should only be handled in small quantity and with great care [2].
See other DIALKYL PEROXIDES

0920. Ethylene glycol (1,2-Ethanediol)

[107-21-1] **$C_2H_6O_2$**



FPA H47, 1976; *HCS 1980*, 483; *RSC Lab. Hazards Data Sheet No. 69*, 1988

Dimethyl terephthalate, Titanium butoxide
See Dimethyl terephthalate: Ethylene glycol, Titanium butoxide

Other reactants
Yoshida, 1980, 48
MRH values calculated for 15 combinations with oxidants are given.

Oxidants MRH values show % of oxidant

1. Oouchi, H. *et al., Chem. Abs.*, 1982, **97**, 8605
2. Inoue, Y. *et al., Chem. Abs.*, 1987, **107**, 120353

In a study of hypergolic ignition of ethylene glycol by oxidants, chromium trioxide, potassium permanganate and sodium peroxide caused ignition on contact at ambient temperature, and ammonium dichromate, silver chlorate, sodium chlorite and uranyl nitrate at 100°C [1]. Results from an exothermicity test in which 1 g portions each of a glycol and an oxidising agent were mixed at 100°C in a Dewar flask were compared with those from DTA experiments [2].

See Chromium trioxide: Ethylene glycol	MRH 2.47/84
Perchloric acid: Glycols and their ethers	MRH 5.69/70
Potassium dichromate: Ethylene glycol	MRH 1.46/89

See Sodium hypochlorite: Ethanediol

Phosphorus pentasulfide

See Tetraphosphorus decasulfide: Alcohols

Silvered copper wire

1. Downs, W. R., *TN D-4327*, Washington, NASA Tech. Note, 1968
2. Stevens, H. D., *Chem. Abs.*, 1975, **83**, 134485

Contact of aqueous ethylene glycol solutions with d.c.-energised silvered copper wires causes ignition of the latter. Bare copper or nickel- or tin-plated wires were inert and silver-plated wire can be made so by adding benzotriazole as a metal deactivator to the coolant solution [1]. This problem of electrical connector fires in aircraft has been studied in detail to identify the significant factors [2].

Sodium hydroxide

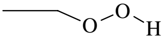
See Sodium hydroxide: Glycols, and Sodium 2-hydroxyethoxide

Sodium hypochlorite

See Sodium hypochlorite: Ethanediol

0921. Ethyl hydroperoxide

[3031-74-1] **$C_2H_6O_2$**



Baeyer, A. *et al., Ber.*, 1901, **34**, 738

It explodes violently on superheating; the barium salt is heat- and impact-sensitive.

Hydriodic acid

Sidgwick, 1950, 873

The concentrated acid (a reducer) is oxidised explosively.

See other REDOX REACTIONS

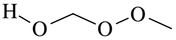
Silver

Sidgwick, 1950, 873

Finely divided ('molecular') silver decomposes the hydroperoxide, sometimes explosively.
See other ALKYL HYDROPEROXIDES

0922. Hydroxymethyl methyl peroxide

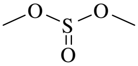
[ ] **$C_2H_6O_3$**



Rieche, A. *et al., Ber.*, 1929, **62**, 2458
Violently explosive, impact-sensitive when heated.
See other 1-OXYPEROXY COMPOUNDS

0923. Dimethyl sulfite

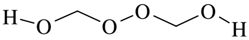
[616-42-2] **$C_2H_6O_3S$**



Phosphorus (III) oxide
See Tetraphosphorus hexaoxide: Organic liquids
See other SULFUR ESTERS

0924. Bis(hydroxymethyl) peroxide

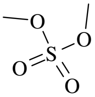
[17088-73-2] **$C_2H_6O_4$**



Wieland, H., *et al., Ber.*, 1930, **63**, 66
Highly explosive and very friction-sensitive. Higher homologues are more stable.
See other 1-OXYPEROXY COMPOUNDS

†0925. Dimethyl sulfate

[77-78-1] **$C_2H_6O_4S$**



(*MCA SD-19*, 1966); *HCS 1980*, 434

Ammonia
1. Lindlar, H., *Angew. Chem.*, 1963, **75**, 297
2. Claesson, P. *et al., Ber.*, 1880, **13**, 1700

A violent reaction occurred which shattered the flask when litre quantities of dimethyl sulfate and conc. aqueous ammonia were accidentally mixed. Use dilute ammonia in

small quantities to destroy dimethyl sulfate [1]. Similar incidents were noted previously with ammonia and other bases [2].
See Tertiary bases, below
See other AMINATION INCIDENTS

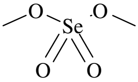
Barium chlorite
See Barium chlorite: Dimethyl sulfate

Other reactants
Yoshida, 1980, 395
MRH values calculated for 13 combinations with oxidants are given.

Tertiary bases
Sorbe, 1968, 123
In absence of diluent, quaternation of some tertiary organic bases may proceed explosively.
See Ammonia, above

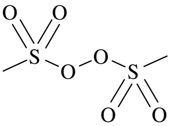
Unnamed material
MCA Case History No. 1786
The product of methylating an unnamed material at 110°C was allowed to remain in the reactor of a pilot plant. and after 80 min the reactor exploded. This was ascribed to exothermic decomposition of the mixture above 100°C, and subsequent acceleration and boiling decomposition at 150°C.
See other SULFUR ESTERS

0926. Dimethyl selenate
[6918-51-0] **$C_2H_6O_4Se$**



Sidgwick, 1950, 977
Dimethyl selenate, like its ethyl and propyl homologues, can be distilled under reduced pressure, but explodes at around 150°C under ambient pressure, though less violently than the lower alkyl nitrates.
See related SULFUR ESTERS

0927. Dimethanesulfonyl peroxide
[1001-62-3] **$C_2H_6O_6S_2$**

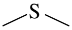


Haszeldine, R. N. *et al., J. Chem. Soc.*, 1964, 4903

A sample heated in a sealed tube exploded violently at 70°C. Unconfined, the peroxide decomposed (sometimes explosively) immediately after melting at 79°C.
See other DIACYL PEROXIDES

†0928. Dimethyl sulfide (Thiobismethane)

[75-18-3] **C_2H_6S**



Butyllithium, Sodium *tert.* butoxide
See Butyllithium, Sodium *tert.* butoxide: Dimethyl sulfide

Dibenzoyl peroxide
See Dibenzoyl peroxide: Dimethyl sulfide

1,4-Dioxane, Nitric acid
See Nitric acid: Dimethyl sulfide, 1,4-Dioxane

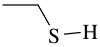
Other reactants
Yoshida, 1980, 389
MRH values calculated for 14 combinations with oxidants are given.

Oxygen
See Oxygen (Gas): Dimethyl sulfide

Xenon difluoride
See Xenon difluoride: Dimethyl sulfide

†0929. Ethanethiol

[75-08-1] **C_2H_6S**

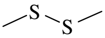


HCS 1980, 497

Other reactants
Yoshida, 1980, 44
MRH values calculated for 14 combinations with oxidants are given.
See other ALKANETHIOLS

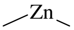
†0930. Dimethyl disulfide

[624-92-0] **$C_2H_6S_2$**



0931. Dimethylzinc

[544-97-8] **C_2H_6Zn**



Air, or Oxygen

1. Egerton, A. *et al., Proc. R. Soc.*, 1954, **A225**, 429
2. Frankland, E., *Phil. Trans. R. Soc.*, 1852, 417

It ignites in air (owing to peroxide formation) [1], and explodes in oxygen [2]. It is slightly endothermic (ΔH_f° (l) +25.1 kJ/mol, 0.26 kJ/g).

2,2-Dichloropropane

Houben-Weyl, 1973, Vol. 13.2a, 767

Uncontrolled reaction is explosive.

See other DIALKYLZINCS: ALKYL CHLORIDES

Ozone

See Ozone: Alkylmetals

Water

Leleu, *Cahiers*, 1977, (88), 371

Reaction is explosively violent.

See other ALKYLMETALS, DIALKYLZINCS, ENDOTHERMIC COMPOUNDS

0932. Dimethylaluminium hydride

[865-37-2] **C_2H_7Al**

Houben-Weyl, 1970, Vol. 13.4, 58

Slight contact with air or moisture causes ignition.

See other ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

0933. Dimethylarsine

[593-57-7] **C_2H_7As**

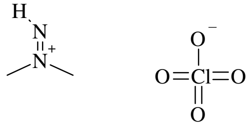
1. von Schwartz, 1918, 322
2. Sidgwick, 1950, 762

It inflames in air [1], even at 0°C [2].

See other ALKYLNON-METAL HYDRIDES

0934. 1,1-Dimethyldiazenium perchlorate

[53534-20-6] (ion) **$C_2H_7ClN_2O_4$**



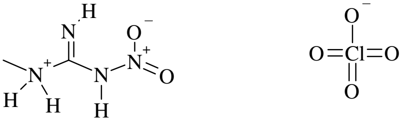
McBride, W. E. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 576 footnote 16

The salt is impact sensitive.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

0935. 1-Methyl-3-nitroguanidinium perchlorate

[ ] **$C_2H_7ClN_4O_6$**



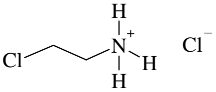
McKay, A. F. *et al., J. Amer. Chem. Soc.*, 1947, **69**, 3029

The salt is sensitive to impact, exploding violently.

See other N—NITRO COMPOUNDS, PERCHLORATE SALTS OF NITROGENOUS BASES

0936. 2-Chloroethylammonium chloride (2-Chloroethylamine hydrochloride)

[870-24-6] **$C_2H_7Cl_2N$**



Alkali

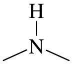
1. Wystrach, V. P. *et al., J. Amer. Chem. Soc.*, 1955, **77**, 5915
2. Wystrach, V. P. *et al., Chem. Eng. News*, 1956, **34**, 1274

The procedure described previously [1] for the preparation of ethylenimine is erroneous. 2-Chloroethylammonium chloride must be added with stirring as a 33% solution in water to strong sodium hydroxide solution. Addition of the solid salt to the alkali caused separation in bulk of 2-chloroethylamine, which polymerised explosively. Adequate dilution and stirring, and a temperature below 50°C are all essential [2].

See other POLYMERISATION INCIDENTS

†0937. Dimethylamine (*N*-Methylmethanamine)

[124-40-3] **C_2H_7N**



(*MCA SD-57*, 1955); *HCS 1980*, 421 (40% solution)

Acrylaldehyde
See Acrylaldehyde: Acids, etc.

4-Chloroacetophenone
See 4-Chloroacetophenone: Dimethylamine

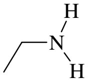
Fluorine MRH 10.6/77
See Fluorine: Nitrogenous bases

Maleic anhydride
See Maleic anhydride: Bases, etc.

Other reactants
Yoshida, 1980, 169
MRH values calculated for 14 combinations with oxidants are given.
See other ORGANIC BASES

†0938. Ethylamine (Ethanamine)

[75-04-7] **C_2H_7N**

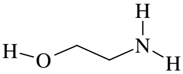


FPA H67, 1978; *HCS 1980*, 467 (cylinder)

Cellulose nitrate
See CELLULOSE NITRATE: AMINES
See other ORGANIC BASES

0939. 2-Hydroxyethylamine (Ethanolamine)

[141-43-5] **C_2H_7NO**



HCS 1980, 457

Acetonitrile, Steel, Water

1. Cheung, T. L., *Chem. Brit.*, 2002, **38**(7), 20
2. Editor's comment

A mixture of acetonitrile, ethanolamine, water, methanol and petroleum ether pressurised and burst the steel waste solvent drum in which it was stored overnight [1]. There appear two possibilities. Reaction of the nitrile with ethanolamine, which releases ammonia and is exothermic, but normally too slow to be hazardous - a catalyst of some sort would be needed. Or the chelating powers of ethanolamine may speed corrosion of the steel generating hydrogen [2].

Carbon dioxide, Pyrophoric deposits

1. Bond, J., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 37—44, Oxford, Pergamon, 1987
2. Bond, J., *Loss Prev. Bull.*, 1995, **121**, 18

Ethanolamine has a large affinity for carbon dioxide, and is used to remove it from process gas streams. A storage tank used to hold the amine had a steel steam coil to warm the contents, and the coil developed a pyrophoric deposit, probably from contact with sulfur-containing impurities. When part of the coil was not covered by the amine, the surface deposit caused a fire which ignited some of the ethanolamine in the closed tank until the air was exhausted and the fire went out. The combined effect of cooling of the hot gases in the tank and of the rapid absorption of the carbon dioxide produced in the fire caused a significant pressure reduction and the tank collapsed [1]. It was also suggested that the pyrophoric material might have been tris(hydroxyethylamine)iron(0), a rather improbable species, or tris(aminoethoxy)iron(III) trihydrate which is perhaps more probable, though its postulated decomposition to pyrophoric iron is less so [2].

See PYROPHORIC IRON—SULFUR COMPOUNDS

Cellulose nitrate

See CELLULOSE NITRATE: AMINES

N,N-Dimethyl-*N,N*-dinitrosoterephthalamide

See N,N′-Dimethyl-*N,N′*-dinitrosoterephthalamide: 2-Hydroxyethylamine

Other reactants

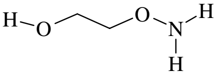
Yoshida, 1980, 370

MRH values calculated for 15 combinations are given.

See other ORGANIC BASES

0940. *O*-(2-Hydroxyethyl)hydroxylamine

[3279-95-6] **$C_2H_7NO_2$**



Sulfuric acid

Campbell, H. F., *Chem. Eng. News*, 1975, **53**(49), 5

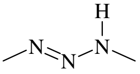
After 30 min at 120°C under vacuum, an equimolar mixture with the conc. acid exploded violently. Salts of unsubstituted hydroxylamine are thermally unstable.

See HYDROXYLAMINIUM SALTS

See other N—O COMPOUNDS

0941. 1,3-Dimethyltriazene (‘Diazoaminomethane’)

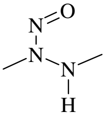
[3585-32-8] **$C_2H_7N_3$**



Dimroth, O., *Ber.*, 1906, **39**, 3910
A drop explodes sharply in contact with flame.
See other TRIAZENES

0942. 1,2-Dimethylnitrosohydrazine

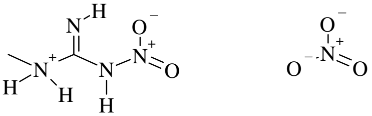
[101672-10-0] **$C_2H_7N_3O$**



Smith, 1966, Vol. 2, 459
The liquid deflagrates on heating.
See other NITROSO COMPOUNDS

0943a. 1-Methyl-3-nitroguanidinium nitrate

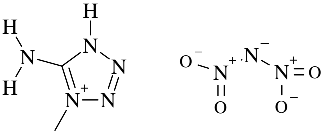
[ ] **$C_2H_7N_5O_5$**



McKay, A. F. *et al., J. Amer. Chem. Soc.*, 1947, **69**, 3029
The salt could be exploded by impact between steel surfaces.
See other N—NITRO COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

0943b. 1,5,-Diamino-4-methyltetrazolium dinitramide

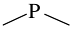
[ ] **$C_2H_7N_9O_4$**



Klapötke, T. M. *et al., J. Amer. Chem. Soc.*, 2005, **127**(7), 2032
Warning is given that dinitramides and aminotetrazoles tend to be explosive - this combination proved highly friction sensitive.
See also Dinitramine
See also HYDRAZINIUM SALTS
See other TETRAZOLES

0944. Dimethylphosphine

[676-59-5] **C_2H_7P**

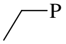


1. Houben-Weyl, 1963, Vol. 12.1, 69
2. Parshall, G. W., *Inorg. Synth.*, 1968, **11**, 158
3. Trenkle, A. *et al., Inorg. Synth.*, 1982, **21**, 180—181

Secondary lower-alkylphosphines readily ignite in air [1]; preparative precautions are detailed [2,3].

See other ALKYLPHOSPHINES

0945. Ethylphosphine
[593-68-0] **C_2H_7P**



Houben-Weyl, 1963, Vol. 12.1, 69

Primary lower-alkylphosphines readily ignite in air.

Halogens, or Nitric acid

von Schwartz, 1918, 324—325

It explodes on contact with chlorine, bromine or fuming nitric acid, and inflames with conc. acid.

See other ALKYLPHOSPHINES

0946. Dimethylammonium perchlorate
[14488-49-4] **$C_2H_8ClNO_4$**

1. Gore, P. H., *Chem. Brit.*, 1976, **12**, 205
2. Menzer, M. *et al., Z. Chem.*, 1977, **17**, 344
3. Gore, P. H. *et al., Synth. Commun.*, 1980, **10**, 320

A violent explosion occurred during vacuum evaporation of an aqueous mixture of excess dimethylamine and perchloric acid [1], and a similar incident occurred when the moist solid from a like preparation was moved [2]. Use of this explosive salt as an intermediate for the preparation of 3-dimethylamino-2-propenylidenedimethylimmonium perchlorate should be avoided, the methylsulfate or triflate salts being preferred [3].

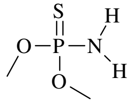
See other PERCHLORATE SALTS OF NITROGENOUS BASES

0947a. 2-Hydroxyethylaminium perchlorate (Ethanolamine perchlorate)
[38092-76-1] **$C_2H_8ClNO_5$**

Annikov, V. E. *et al., Chem. Abs.*, 1983, **99**, 160860

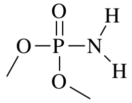
Ethanolamine perchlorate was outstanding amongst other nitrogenous perchlorate salts for its capacity for detonation as an aqueous solution.
See other PERCHLORATE SALTS OF NITROGENOUS BASES

0947b. Dimethyl phosphoramidothionate
[17321-47-0] **$C_2H_8NO_2PS$**



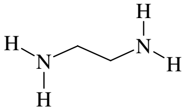
Wakakura, M. *et al., J. Loss Prev. Process Ind.*, 1999, **12**, 79
Due to pump failure this insecticide intermediate was stored longer and warmer than usual. It decomposes from 99°C, presumably by (base catalysable) intermolecular rearrangement via the imidothiolate tautomer to the O,S-dimethylphosphoramidothioate, which will itself be somewhat unstable. Result, an exploding storage tank spewing its toxic contents. [Note: between translation and chemical engineering origin, the original paper is somewhat confused, the names not agreeing with the structures, this account follows the structures.
See other PHOSPHORUS ESTERS, THIONOESTERS

0948. Dimethyl phosphoramidate
[2697-42-9] **$C_2H_8NO_3P$**



Chlorine
See Chlorine: Dimethyl phosphoramidate
See other PHOSPHORUS ESTERS

0949. 1,2-Diaminoethane (Ethylenediamine)
[107-15-3] **$C_2H_8N_2$**



Cellulose nitrate
See CELLULOSE NITRATE: Amines

Diisopropyl peroxydicarbonate
See Diisopropyl peroxydicarbonate: Amines, etc.

Nitromethane
See Nitromethane: Acids, etc., and: 1,2-Diaminoethane, etc.

Other reactants

Yoshida, 1980, 50

MRH values calculated for 13 combinations with oxidants are given.

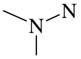
Silver perchlorate

See Silver perchlorate: 1,2-Diaminoethane

See other ORGANIC BASES

†0950. 1,1-Dimethylhydrazine

[57-14-7] **$C_2H_8N_2$**



HCS 1980, 431

Energy of decomposition (in range 280—380°C) measured as 1.15 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Dichloromethane

See Dichloromethane: 1,2-Diaminoethane

Dicyanofurazan

See Dicyanofurazan: Nitrogenous bases

Oxidants

1. Kirk-Othmer, 1966, Vol. 11, 186
2. Wannagat, U. *et al., Monatsh.*, 1969, **97**, 1157—1162
3. *491M*, 1975, 158

A powerful reducing agent and fuel, hypergolic with many oxidants, such as dinitrogen tetraoxide, hydrogen peroxide and nitric acid [1]. The ignition delay with fuming nitric acid was determined as 8 ms, explosion also occurring [2]. When spread (as a thin film, or absorbed on porous or fibrous material) to expose a large surface to air, ignition may occur [3].

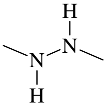
See Hexanitroethane: 1,1-Dimethylhydrazine,

See also ROCKET PROPELLANTS

See other ORGANIC BASES, REDUCANTS

†0951. 1,2-Dimethylhydrazine

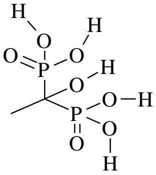
[540-73-8] **$C_2H_8N_2$**



See other ORGANIC BASES, REDUCANTS

0952. 1-Hydroxyethylidene-1,1-diphosphonic acid

[2809-21-4] **$C_2H_8O_7P_2$**



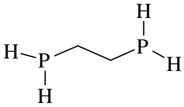
'Data Sheet ADPA 60A', Oldbury, Albright & Wilson, 1977

The anhydrous acid decomposes, often violently, at above 200°C, to give phosphine, phosphoric acid and other products.

See other ORGANIC ACIDS

0953. 1,2-Diphosphinoethane

[5518-62-7] **$C_2H_8P_2$**



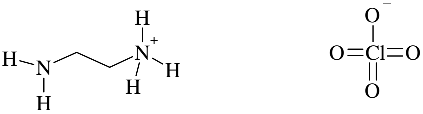
Taylor, R. C. *et al., Inorg. Chem.*, 1973, **14**, 10—11

It ignites in air.

See other ALKYLPHOSPHINES

0954. 2-Aminoethylammonium perchlorate

[25682-07-9] **$C_2H_9ClN_2O_4$**



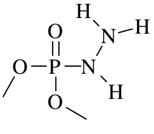
Hay, R. W. *et al., J. Chem. Soc., Dalton Trans.*, 1975, 1467

Solutions of the perchlorate salts of 1,2-diaminoethane and other amines must be evaporated without heating to avoid the risk of violent explosions.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

0955. Dimethyl hydrazidophosphate (Dimethylphosphorohydrazine)

[58816-61-8] **$C_2H_9N_2O_3P$**



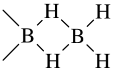
Anon., *Sichere Chemiearbeit*, 1990, **42**, 56

The compound decomposed explosively upon vacuum distillation at 150°C. Caution is advised with similar hydrazides.

See related PHOSPHORUS ESTERS

†0956. 1,1-Dimethyldiborane

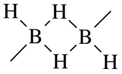
[16924-32-6] **$C_2H_{10}B_2$**



See other ALKYLBORANES

†0957. 1,2-Dimethylborane

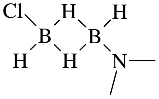
[17156-88-6] **$C_2H_{10}B_2$**



See other ALKYLBORANES

0958. *B*-Chlorodimethylaminodiborane

[ ] **$C_2H_{10}B_2ClN$**



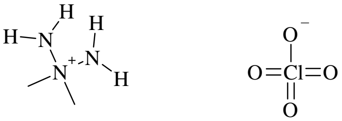
Burg, A. B. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 3454

It ignites in air.

See related BORANES, HALOBORANES

0959. 2,2-Dimethyltriazanium perchlorate

[20446-69-9] **$C_2H_{10}ClN_3O_4$**

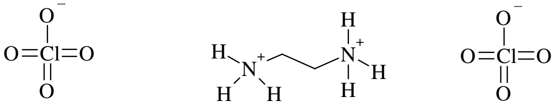


Rubtsov, Yu. I. *et al., Chem. Abs.*, 1981, **95**, 117860

It decomposes rapidly above 122°C.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

0960. 1,2-Ethylenebis(ammonium) perchlorate
[15718-71-5] **$C_2H_{10}Cl_2N_2O_8$**

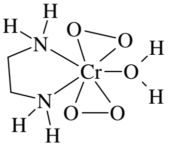


Lothrop, W. C. *et al., Chem. Rev.*, 1949, **44**, 432

An explosive which appreciably exceeds the power and brisance of TNT.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

0961. Aqua-1,2-diaminoethanediperoxochromium(IV)
[17168-82-0] **$C_2H_{10}CrN_2O_5$**

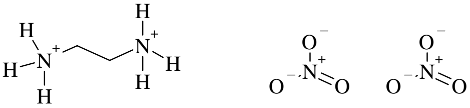


1. Childers, R. F. *et al., Inorg. Chem.*, 1968, **7**, 749
2. House, D. A. *et al., Inorg. Chem.*, 1966, **5**, 840

The monohydrate is light-sensitive and explodes at 96—97°C if heated at 2°/min [1]. It effervesces vigorously on dissolution in perchloric acid [2].

See other AMMINECHROMIUM PEROXOCOMPLEXES

0962a. 1,2-Diammonioethane nitrate (Ethylenediamine dinitrate)
[20829-66-7] **$C_2H_{10}N_4O_6$**

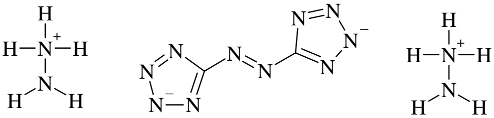


Dobratz, B. M., *Chem. Abs.*, 1984, **100**, 88163

Ethylenediamine dinitrate was formerly used as a military explosive.

See other OXOSALTS OF NITROGENOUS BASES

0962b. Dihydrazinium 5,5′-azobistetrazolate
[354986-08-6] [354986-08-6] **$C_2H_{10}N_{14}$**

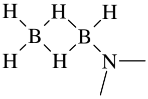


Klapoetke, T. M., *et al., Inorg. Chem.*, 2001, **40**(14), 3570

The simple salt, its dihydrate and its dihydrazinate, were prepared and isolated. Stable at room temperature, but not above 100°C, and almost insensitive to shock and friction violent detonation ensues on rapid heating, or with an initiator.
See other HIGH-NITROGEN COMPOUNDS, TETRAZOLES

0963. Dimethylaminodiborane

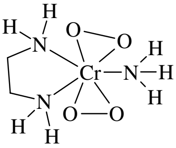
[23273-02-1] **$C_2H_{11}B_2N$**



Keller, P. G., *Inorg. Synth.*, 1977, **17**, 34
It ignites in air, like the parent diborane.
See related BORANES

0964. Ammine-1,2-diaminoethanediperoxochromium(IV)

[17168-82-0] **$C_2H_{11}CrN_3O_4$**

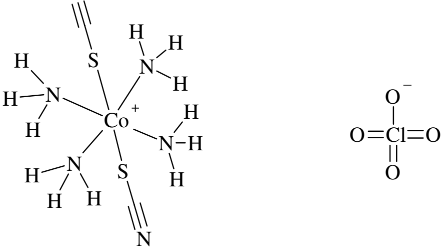


House, D. A. *et al., Inorg. Chem.*, 1967, **6**, 1077
The monohydrate is potentially explosive at 25°C and decomposes or explodes at 115° during slow or moderate heating.

Hydrogen bromide
Hughes, R. G. *et al., Inorg. Chem.*, 1968, **7**, 74
Interaction must be slow with cooling to prevent explosion.
See other AMMINECHROMIUM PEROXOCOMPLEXES

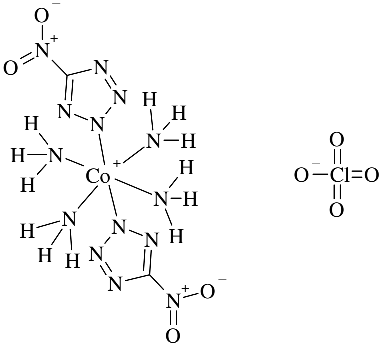
0965. Tetraamminedithiocyanatocobalt(III) perchlorate

[36294-69-6] (ion) **$C_2H_{12}ClCoN_6O_4S_2$**



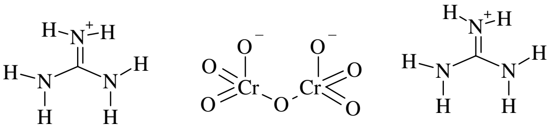
Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 375
Explodes at 335°C, medium impact-sensitivity.
See other AMMINEMETAL OXOSALTS

0966. Tetraamminebis(5-nitro-2*H*-tetrazolato)cobalt(1+) perchlorate
[117412-28-9] **$C_2H_{12}ClCoN_{14}O_8$**



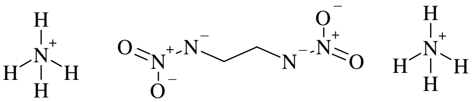
Fronabarger, J. W., *et al., Proc. Int. Pyrotech. Semin.*, 1996, **22nd**, 645
It is being developed as an initiating explosive.
See other AMMINEMETAL OXOSALTS, TETRAZOLES

0967. Guanidinium dichromate
[27698-99-3] **$C_2H_{12}Cr_2N_6O_7$**



Ma, C., *J. Amer. Chem. Soc.*, 19512, **73**, 1333—1335
Heating causes orderly decomposition, but under confinement, a violent explosion.
See other DICHROMATE SALTS OF NITROGENOUS BASES

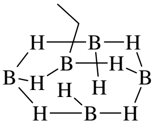
0968. Ammonium 1,2-ethylenebis(nitramide)
[3315-89-7] **$C_2H_{12}N_6O_4$**



Violent decomposition occurred at 191°C.
See entry DIFFERENTIAL THERMAL ANALYSIS (reference 1)
See other N—NITRO COMPOUNDS

0969. Ethylpentaborane(9)

[28853-06-7] **$C_2H_{13}B_5$**



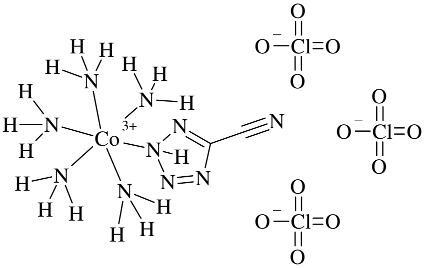
Leleu, *Cahiers*, 1977, (88), 365

It ignites in air.

See other ALKYLBORANES

0970. 2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate

[70247-32-4] **$C_2H_{16}Cl_3CoN_{10}O_{12}$**



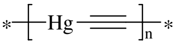
Loyola, V. M. *et al., Chem. Abs.*, 1981, **95**, 222342

It is a practical explosive of zero oxygen balance, but much less sensitive to accidental explosion than conventional detonators.

See other AMMINEMETAL OXOSALTS, TETRAZOLES

0971. Mercury(II) acetylide

[37297-87-3] **$(C_2Hg)_n$**



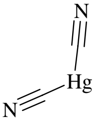
Bailar, 1973, Vol. 3, 314—315

Possibly polymeric, it explodes when heated or shocked.

See other MERCURY COMPOUNDS, METAL ACETYLIDES

0972. Mercury(II) cyanide

[592-04-1] **C_2HgN_2**



Ullmann, A8, 176

It is a moderately endothermic compound but of high MW (ΔH_f° (s) +261.5 kJ/mol, 1.035 kJ/g). It may explode if detonated, although it is used as an inerting diluent for the more sensitive and more powerful oxycyanide, $Hg(CN)_2.HgO$.

Fluorine

See Fluorine: Metal salts

Hydrogen cyanide

Wöhler, L. *et al., Chem. Ztg.*, 1926, **50**, 761

The cyanide is a friction- and impact-sensitive explosive, and may initiate detonation of liquid hydrogen cyanide. Other heavy metal cyanides are similar.

Magnesium

See Magnesium: Metal cyanides

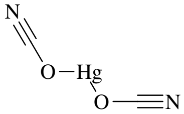
Sodium nitrite

See Sodium nitrite: Metal cyanides

See other ENDOTHERMIC COMPOUNDS, MERCURY COMPOUNDS, METAL CYANIDES

0973. Mercury(II) cyanate

[3021-39-4] **$C_2HgN_2O_2$**



1. Editor's comments
2. Biasutti, 1981, 53

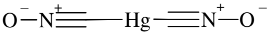
Two explosions during the crushing of the cyanate are recorded [1]. Once the standard preparation of cyanogen (qv) was by pyrolysis of this salt – the method was abandoned after explosions attributed to fulminate impurities. Now that the structure of fulminates has been established, isomerisation of cyanate to give fulminate as impurity is no longer credible [2].

See other MERCURY COMPOUNDS

See related METAL CYANIDES (AND CYANO COMPLEXES)

0974. Mercury(II) fulminate

[628-86-4] **$C_2HgN_2O_2$**



NSC 309, 1978

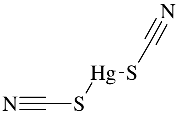
Alone, or Sulfuric acid

1. Urbanski, 1967, Vol. 3, 135, 140
2. Carl, L. R., *J. Franklin Inst.*, 1945, **240**, 149

Mercury fulminate, readily formed by interaction of mercury(II) nitrate, nitric acid and ethanol, is endothermic (ΔH_f° (s) +267.7 kJ/mol, 0.94 kJ/g) and was a very widely used detonator. It may be initiated when dry by flame, heat, impact, friction or intense radiation. Contact with sulfuric acid causes explosion [1]. The effects of impurities on the preparation and decomposition of the salt have been described [2].

See other ENDOTHERMIC COMPOUNDS, MERCURY COMPOUNDS, METAL FULMINATES

0975. Mercury(II) thiocyanate
[592-85-8] **$C_2HgN_2S_2$**



HCS 1980, 619

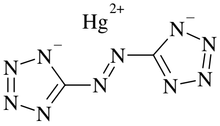
Unpublished information, 1950

It is a moderately endothermic and thermally unstable compound of high MW (ΔH_f° (s) +200.8 kJ/mol, 0.63 kJ/g). A large batch of the damp salt became overheated in a faulty steam drying oven, and decomposed vigorously, producing an enormous 'Pharaoh's serpent'.

See other ENDOTHERMIC COMPOUNDS, MERCURY COMPOUNDS

See related METAL CYANIDES (AND CYANO COMPLEXES)

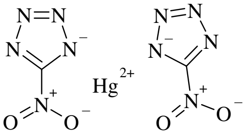
0976. Mercury 5,5′-azotetrazolide
[87552-19-0] **C_2HgN_{10}**



See entry METAL AZOTETRAZOLIDES

See other MERCURY COMPOUNDS, TETRAZOLES

0977. Mercury(II) 5-nitrotetrazolide
[60345-95-1] **$C_2HgN_{10}O_4$**



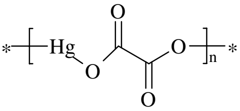
1. Gilligan, W. H. *et al., Rept.AD-A036086*, Richmond (Va.), USNTIS, 1976
2. Farncomb, R. E. *et al., Chem. Abs.*, 1977, **87**, 203672
3. Redman, L. D. *et al. Chem. Abs.*, 1984, **100**, 194540

It is a promising replacement for lead azide in detonators [1], and a remotely controlled procedure for the preparation of this oxygen-balanced compound is described [2]. Preparative methods have been assessed for safety features [3].

See other MERCURY COMPOUNDS, C—NITRO COMPOUNDS, TETRAZOLES

0978. Mercury(II) oxalate

[3444-13-1] **C_2HgO_4**



1. Anon., *ABCM Quart. Safety Summ.*, 1953, **24**, 30, 45
2. Muir, G. D., private comm., 1968

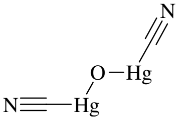
When dry, the oxygen-balanced salt explodes readily on percussion, grinding or heating to 105°C. This instability is attributed to presence of impurities (nitrate, oxide, or basic oxalate) in the product [1]. It is so thermally unstable that storage is inadvisable [2].

See entry OXYGEN BALANCE

See other CATALYTIC IMPURITY INCIDENTS, MERCURY COMPOUNDS, METAL OXALATES

0979. Dimercury dicyanide oxide (Mercury(II) oxycyanide)

[1335-31-5] **C_2Hg_2O**



1. Merck Index, 1983, 840; *ibid.* 1989, 5781
2. Kast, H. *et al., Chem. Abs.*, 1922, **16**, 4065
3. *MCA Guide*, 1972, 309

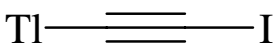
The compound is explosive when pure, and sensitive to impact or heat. It is stabilised for commerce by the presence of a major excess of mercury(II) cyanide [1]. Several explosive incidents have been described [2], most involving friction [3].

See other FRICTIONAL INITIATION INCIDENTS, MERCURY COMPOUNDS

See related METAL CYANIDES (AND CYANO COMPLEXES)

0980. Thallium(I) iodacetylide

[ ] **C_2ITl**

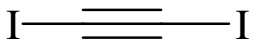


Fawcett, H. H., private comm., 1984

The acetylide, produced as an unexpected major product, is a shock- and friction-sensitive explosive. A few mg exploded when touched with a spatula, and the remaining 2 g sample detonated violently when destroyed by a controlled explosion.
See other HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

0981. Diiodoacetylene (Diiodoethyne)

[624-74-8] **C_2I_2**

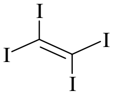


1. Anon., *Sichere Chemiearb.*, 1955, **7**, 55
2. Vaughn, T. H. *et al., J. Amer. Chem. Soc.*, 1932, **54**, 789
3. Taylor, G. N., *Chem. Brit.*, 1981, **17**, 107

Pure recrystallised material exploded while being crushed manually in a mortar. The decomposition temperature is 125°C, and this may have been reached locally during crushing [1]. Explosion on impact, on heating to 84°C, and during attempted distillation at 98°C/5 mbar had been recorded previously [2]. During an attempt to repeat the published preparation [2], a relatively large amount of the very sensitive explosive, nitrogen triiodide (ibid.), was isolated [3].
See other HALOACETYLENE DERIVATIVES

0982. Tetraiodoethylene

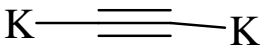
[513-92-8] **C_2I_4**



Iodine pentafluoride
See Iodine pentafluoride: Tetraiodoethylene
See other HALOALKENES, IODINE COMPOUNDS

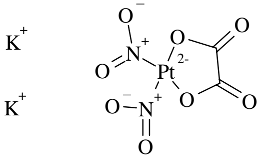
0983. Potassium acetylide

[22754-96-7] **C_2K_2**



Water
Bahme, 1972, 80
Contact with limited amounts of water may cause ignition and explosion of evolved acetylene.
See other METAL ACETYLIDES

0984. Potassium dinitrooxalatoplatinate(2—)
[15213-49-7] **$C_2K_2N_2O_8Pt$**



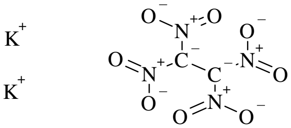
Vèzes, M. *Compt. rend.*, 1897, **125**, 525

The salt decomposes violently at 240°C.

See other PLATINUM COMPOUNDS

See related METAL OXALATES

0985. Potassium 1,1,2,2-tetranitroethanediide
[32607-31-1] **$C_2K_2N_4O_8$**

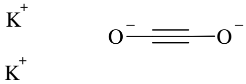


1. Borgardt, F. G. *et al., J. Org. Chem.*, 1966, **31**, 2806, 2810
2. Griffin, T. S. *et al., J. Org. Chem.*, 1980, **45**, 2882

This anhydrous salt, and the mono- and di-hydrates of the analogous lithium and sodium salts, are all very impact-sensitive. The potassium salt, an intermediate in the preparation of hexanitroethane [1], was not allowed to become dry during isolation, but after precipitation was washed with methanol and dichloromethane and used wet with the latter for the succeeding nitration stage [2].

See other POLYNITROALKYL COMPOUNDS

0986. Potassium acetylene-1,2-dioxide (Potassium ethynediolate)
[2851-55-0] **$C_2K_2O_2$**



Air, or Halocarbons, or Halogens, or Protic compounds

Taylor, C. K., *Chem. Abs.*, 1983, **99**, 32105

Produced by action of carbon monoxide on potassium in liquid ammonia at —50°C, the yellow powder burns explosively in contact with air, halocarbons, halogens, alcohols, water and any material with acidic hydrogen. Analogous metal derivatives are reviewed.

See Potassium benzenehexoxide

See other ACETYLENIC COMPOUNDS

0987. Lanthanum carbide

[12071-15-7] **C_2La**

$$\mathrm{La}^{4+}\qquad \mathrm{C}^{2-}\equiv\mathrm{C}^{2-}$$

Borlas, R. A. *et al., Chem. Abs.*, 1976, **84**, 182199

'On the flammability and explosiveness of lanthanum carbide and cerium carbide powders' (title only translated).

See other METAL NON-METALLIDES

0988. Lithium acetylide

[1070-75-3] **C_2Li_2**

$$\mathrm{Li}{-}{\equiv}{-}\mathrm{Li}$$

Halogens

Mellor, 1946, Vol. 5, 848

It burns brilliantly when cold in fluorine or chlorine, but must be warm before ignition occurs in bromine or iodine vapours.

Lead(II) oxide

See Lead(II) oxide: Metal acetylides

Non-metals

Mellor, 1946, Vol. 5, 848

It burns vigorously in phosphorus, selenium or sulfur vapours.

See other METAL ACETYLIDES

0989. Lithium ethynediolate

[88906-07-4] **$C_2Li_2O_2$**

$$\mathrm{Li}^{+}\,\mathrm{O}^{-}{-}{\equiv}{-}\mathrm{O}^{-}\,\mathrm{Li}^{+}$$

Weiss, E., *Angew. Chem. (Int.)*, 1993, **32**(11), 1518

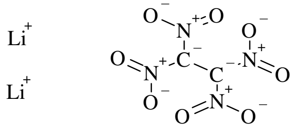
Too shock sensitive to obtain crystallographic data.

See Lithium benzenehexoxide

See other ACETYLENIC COMPOUNDS

0990. Lithium 1,1,2,2-tetranitroethanediide

[ ] **$C_2Li_2N_4O_8$**

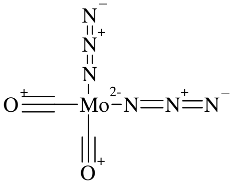


See Potassium 1,1,2,2-tetranitroethanediide

See other POLYNITROALKYL COMPOUNDS

0991. Dicarbonylmolybdenum diazide

[68348-85-6] **$C_2MoN_6O_2$**



Alone, or Water

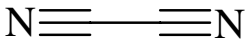
Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 513

This and the tungsten analogue (both homopolymeric) are extremely sensitive, exploding on the slightest mechanical stress, or violently in contact with traces of water.

See related CARBONYLMETALS, METAL AZIDES

†0992. Dicyanogen (Ethanedinitrile) (Cyanogen) (Oxalonitrile)

[460-19-5] **C_2N_2**



Thorpe, E., *Dictionary of Applied Chemistry*, Vol II, 192, London, Longmans Green, 1912

Although the gas is extremely stable to heating, cyanogen is early reported detonable, presumably as liquid, by mercury fulminate. With ΔH_f° (g) +307.9 kJ/mol, 5.91 kJ/g, it is the thermal stability that is the surprise.

Oxidants

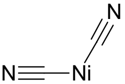
Dicyanogen is extremely endothermic and the potential energy of mixtures with powerful oxidants may be released explosively under appropriate circumstances.

See Dichlorine oxide: Dicyanogen
Fluorine: Halogens
Oxygen (Liquid): Liquefied gases
Ozone: Dicyanogen
ROCKET PROPELLANTS

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

0993. Nickel(II) cyanide

[557-19-7] **C_2N_2Ni**



It is a somewhat endothermic compound (ΔH_f° (s) +113.4 kJ/mol, 1.02 kJ/g), though not notably thermally unstable.

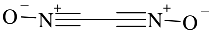
Magnesium

See Magnesium: Metal cyanides

See other ENDOTHERMIC COMPOUNDS, METAL CYANIDES

0994. Dicyanogen *N,N′*-dioxide

[4331-98-0] **$C_2N_2O_2$**



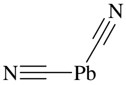
Grundmann, C. J., *Angew. Chem.*, 1963, **75**, 450; *Ann.*, 1965, **687**, 194

The solid decomposes at —45°C under vacuum, emitting a brilliant light before exploding.

See related CYANO COMPOUNDS, HALOGEN OXIDES

0995. Lead(II) cyanide

[592-05-2] **C_2N_2Pb**



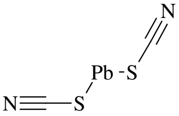
Magnesium

See Magnesium: Metal cyanides

See other METAL CYANIDES

0996. Lead(II) thiocyanate

[592-87-0] **$C_2N_2PbS_2$**



Urbanski, 1967, Vol. 3, 230

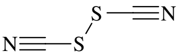
The explosive properties of lead thiocyanate have found limited use.

See other HEAVY METAL DERIVATIVES

See related METAL CYANIDES (AND CYANO COMPLEXES)

0997. Thiocyanogen

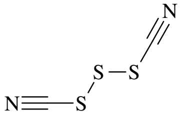
[505-14-6] **$C_2N_2S_2$**



Söderbäck, E., *Ann.*, 1919, **419**, 217

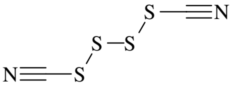
Low-temperature storage is necessary, as it polymerises explosively above its m.p., —2°C (—7°C is also recorded).
See other POLYMERISATION INCIDENTS
See related CYANO COMPOUNDS

0998. Sulfur thiocyanate
[57670-85-6] **$C_2N_2S_3$**



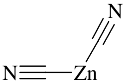
Lecher, H. *et al., Ber.*, 1922, **55**, 1481
It decomposes explosively (but harmlessly) on storage at ambient temperature.
See other N—S COMPOUNDS
See related CYANO COMPOUNDS

0999. Disulfur thiocyanate
[ ] **$C_2N_2S_4$**



Lecher, H. *et al., Ber.*, 1922, **55**, 1485
It melts at —3.5°C and decomposes explosively (but harmlessly) after turning yellow.
See other N—S COMPOUNDS
See related CYANO COMPOUNDS

1000. Zinc cyanide
[557-21-1] **C_2N_2Zn**

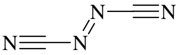


It is modestly endothermic (ΔH_f° (s) +77 kJ/mol, 0.65 kJ/g) but not notably thermally unstable.

Magnesium
See Magnesium: Metal cyanides
See other ENDOTHERMIC COMPOUNDS, METAL CYANIDES

1001. Dicyanodiazene (Azocarbonitrile)

[1557-57-9] **C_2N_4**



1. Marsh, F. D. *et al., J. Amer. Chem. Soc.*, 1965, **87**, 1819
2. Ittel, S. D. *et al., Inorg. Chem.*, 1975, **14**, 1183

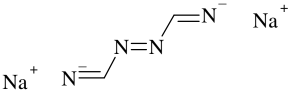
The solid explodes when mechanically shocked or heated in a closed vessel [1]. Preparative methods are hazardous because of the need to heat the explosive precursor, cyanogen azide [1,2].

See CYANONITRENE

See other AZO COMPOUNDS, CYANO COMPOUNDS

1002. Disodium dicyanodiazenide

[ ] **$C_2N_4Na_2$**



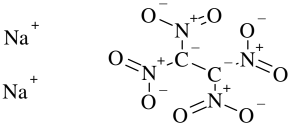
Marsh, F. D. *et al., J. Amer. Chem. Soc.*, 1965, **87**, 1820

The radical anion salt is an explosive powder.

See related AZO COMPOUNDS, CYANO COMPOUNDS

1003. Sodium 1,1,2,2-tetranitroethanediide

[4415-23-0] **$C_2N_4Na_2O_8$**

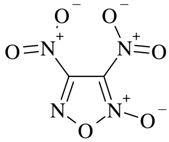


See Potassium 1,1,2,2-tetranitroethanediide

See other POLYNITROALKYL COMPOUNDS

1004. 3,4-Dinitrofurazan-2-oxide

[153498-61-4] **$C_2N_4O_6$**



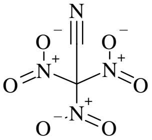
Godovikova, T. L., *Mendeleev Comm.*, 1993, (5) 209

This oxygen rich explosive is claimed to be the first pernitro heterocycle known.

See other FURAZAN N-OXIDES, C—NITRO COMPOUNDS

1005. Trinitroacetonitrile

[630-72-8] **$C_2N_4O_6$**



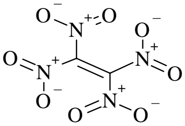
1. Schischkow, A., *Ann. Chim. [3]*, 1857, **49**, 310
2. Parker, C. O. *et al., Tetrahedron*, 1962, **17**, 79, 84

It explodes if heated quickly to 220°C [1]. It is also a friction- and impact-sensitive explosive, which may be used conveniently in carbon tetrachloride solution to minimise handling problems [2].

See other CYANO COMPOUNDS, POLYNITROALKYL COMPOUNDS

1006. Tetranitroethylene

[13223-78-4] **$C_2N_4O_8$**



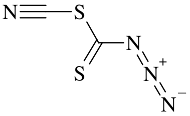
Baum, K, *et al., J. Org. Chem.*, 1985, **50**, 2736—2739

This exceptionally reactive dienophile (at least one order of magnitude greater than tetracyanoethylene) reacted normally with dilute solutions of unsaturated compounds in dichloromethane, but sometimes explosively in absence of solvent.

See other NITROALKENES

1007. Thiocarbonyl azide thiocyanate

[ ] **$C_2N_4S_2$**



1. CHETAH, 1990, 182
2. Editor's comment

Shock sensitive [1]. Given the general tendency of thiocarbonyl azides to cyclise as formed, it is probably not this structure [2].

Ammonia, or Hydrazine

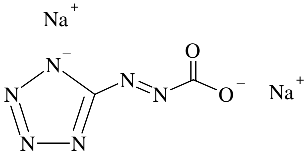
Audrieth, L. F. *et al., J. Amer. Chem. Soc.*, 1930, **52**, 2799—2805

The unstable (undoubtedly endothermic) compound reacts explosively with ammonia gas, and violently with conc. hydrazine solutions.

See other ORGANIC AZIDES
See related CYANO COMPOUNDS

1008. Disodium 5-tetrazolazocarboxylate

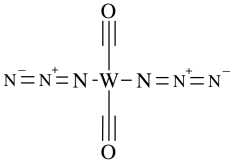
[68594-24-1] **$C_2N_6Na_2O_2$**



Thiele, J. *et al., Ann.*, 1895, **287**, 238
It is explosive.
See other AZO COMPOUNDS, TETRAZOLES

1009. Dicarbonyltungsten diazide

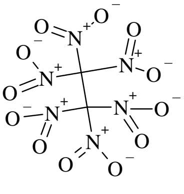
[68379-32-8] **$C_2N_6O_2W$**



Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 513
This and the molybdenum analogue (both homopolymeric) are extremely sensitive, exploding on the slightest mechanical stress, or violently in contact with traces of water.
See related CARBONYLMETALS, METAL AZIDES

1010. Hexanitroethane

[918-37-6] **$C_2N_6O_{12}$**



1. Loewenschuss, A. *et al., Spectrochim. Acta*, 1974, **30A**, 371—378
2. Sorbe, 1968, 149

Grinding the solid to record its IR spectrum was precluded on safety grounds [1]. It decomposes explosively above 140°C [2].

Boron

Finnerty, A. E. *et al., Chem. Abs.*, 1979, **91**, 177486

There is an autocatalytic reaction at ambient temperature in this new explosive combination.

1,1-Dimethylhydrazine

Noble, P. *et al., Am. Inst. Aeron. Astronaut. J.*, 1963, **1**, 395—397

Hexanitroethane is a powerful oxidant and hypergolic with dimethylhydrazine or other strong organic bases.

Organic compounds

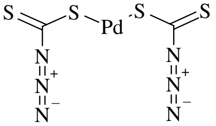
Will, M., *Ber.*, 1914, **47**, 961—965

Though relatively insensitive to friction, impact or shock, it can be detonated. With hydrogen containing organic compounds, this oxygen-rich compound (+200% oxygen balanced) forms powerfully explosive mixtures. The addition compound with 2-nitroaniline ($C_8H_6N_8O_{14}$, —27% balance) is extremely explosive.

See other POLYNITROALKYL COMPOUNDS

1011. Palladium(II) azidodithioformate

[29149-89-1] **$C_2N_6PdS_4$**



Fehlhammer, W. P. *et al., Z. Naturforsch.*, 1983, **38B**, 547

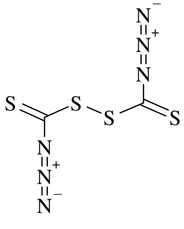
In the first stage of the preparation of bis(triphenylphosphine)palladium(II) isothiocyanate, a large deficiency of aqueous palladium nitrate must be added with rapid stirring to an excess of sodium azidodithioformate solution to avoid the precipitation of explosive palladium(II) azidodithioformate.

See Azidodithioformic acid

See other ACYL AZIDES

1012a. Bis(azidothiocarbonyl) disulfide

[ ] **$C_2N_6S_4$**

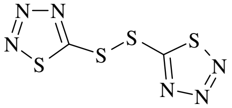


1. Smith, G. B. L., *Inorg Synth.*, 1939, **1**, 81
2. Klapötke, T. M., *et al., Inorg. Chem.*, 2004, **43**(4), 1370

This compound, readily formed by iodine oxidation of azidodithioformic acid or its salts, is a powerful explosive. It is sensitive to mechanical impact or heating to 40°C, and slow decomposition during storage increases the sensitivity. Preparative precautions are detailed [1]. The actual structure is thiatriazolyl disulfide [2].
See Azidodithioformic acid
See other ACYL AZIDES

1012b. Bis(1,2,3,4-thiatriazol-5-yl) disulfide

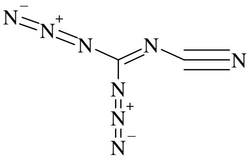
[219797-23-6] **$C2N_6S_4$**



Holm. A., *Comprehensive Heterocyclic Chemistry*, (Ed. Katritzky, A. R.), Vol. 6, Pt 4B, Oxford, Pergamon, 1984
The actual structure of azididodithiocarbonyl disulfide immediately above. It is reported it may explode even under water.

1013a. Diazidomethylenecyanamide

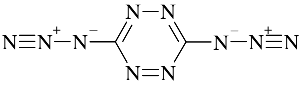
[67880-22-2] **C_2N_8**



Marsh, F. D., *J. Org. Chem.*, 1972, **37**, 2967
This explosive solid may be produced during preparation of cyanogen azide.
See other CYANO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1013b. 3,6-Diazido-1,2,4,5-tetrazine

[5940-58-9] **C_2N_{10}**



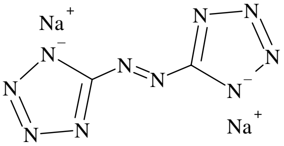
1. Marcus, H. J. *et al., J. Org. Chem.*, 1963, **28**(9), 2372
2. Huynh, M. H. V., *et al., Angew. Chem. (Int.)*, 2004, **43**(42), 5658

Crude material twice detonated spontaneously on exposure to air [1]. This compound is recommended as a precursor to carbon nanospheres and carbon nitrides, obtained by slow heating to 150°C under various atmospheres. It is also recommended that it be not handled in greater than 300 mg quantity, behind a shield, being exceedingly

sensitive to shock, friction and electrostatic discharge. It explodes if heated to pyrolysis temperatures too fast [2].
See other HIGH-NITROGEN COMPOUNDS

1014. Disodium 5,5′-azotetrazolide

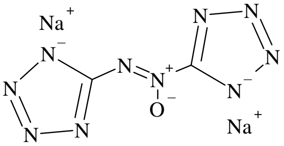
[41463-64-3] **$C_2N_{10}Na_2$**



See entry METAL AZOTETRAZOLIDES
See other TETRAZOLES

1015. Disodium 5,5′-azoxytetrazolide

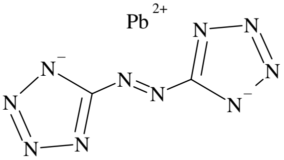
[ ] **$C_2N_{10}Na_2O$**



Thiele, J. *et al., Ann.*, 1893, **273**, 151
Insensitive to friction or impact, but explodes violently on heating in a melting point tube or on analytical combustion, destroying the apparatus in both cases.
See other N-OXIDES, TETRAZOLES
See related METAL AZOTETRAZOLIDES

1016. Lead 5,5′-azotetrazolide

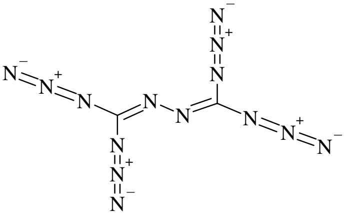
[87489-52-9] **$C_2N_{10}Pb$**



See entry METAL AZOTETRAZOLIDES
See other TETRAZOLES

1017. Diazidomethyleneazine

[ ] C_2N_{14}



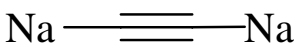
Houben-Weyl, 1965, Vol. 10.3, 793

This very explosive bis-*gem*-diazide contains over 89% of nitrogen.

See other HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1018. Sodium acetylide (Sodium ethynide)

[2881-62-1] C_2Na_2



1. Opolsky, S., *Bull. Acad. Cracow*, 1905, 548
2. Houben-Weyl, 1977, Vol. 5.2a, 361

A brown explosive form is produced if excess sodium is used in preparation of thiophene homologues — possibly because of sulfur compounds [1]. As normally produced, it is a dry stable solid, but material prepared from acetylene and sodium—oil dispersions ignites in air [2].

Halogens

Mellor, 1946, Vol. 5, 848

Sodium acetylide burns in chlorine and (though not stated) probably also in fluorine, and in contact with bromine and iodine on warming.

Metal salts

Mellor, 1946, Vol. 5, 848

Rubbing in a mortar with some metal chlorides or iodides may cause incandescence or explosion. Sulfates are reduced, and nitrates would be expected to behave similarly.

Metals

Mellor, 1946, Vol. 5, 848

Trituration in a mortar with finely divided aluminium, iron, lead or mercury may be violent, carbon being liberated.

Non-metal oxides

von Schwartz, 1918, 328

Sodium acetylide incandesces in carbon dioxide or sulfur dioxide.

Oxidants

Mellor, 1946, 5, 848

Ignites on warming in oxygen, and incandesces at 150°C in dinitrogen pentaoxide.

See Halogens, above

Phosphorus

See Phosphorus: Metal acetylides

Water

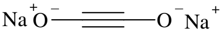
1. Mellor, 1946, Vol. 5, 848
2. Davidsohn, W. E., *Chem. Rev.*, 1967, **67**, 74

Excess water is necessary to prevent explosion [1]; the need for care in handling is stressed [2].

See other METAL ACETYLIDES

1019. Sodium ethynediolate

[2611-42-9] **$C_2Na_2O_2$**

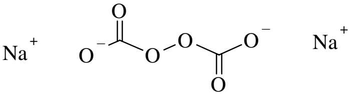


See Sodium: Non-metal oxides

See other ACETYLENIC COMPOUNDS

1020. Sodium peroxydicarbonate

[3313-92-6] **$C_2Na_2O_6$**



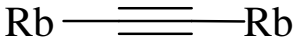
Acetic anhydride

See Sodium carbonate hydrogen peroxide: Acetic anhydride

See other PEROXOACID SALTS

1021. Rubidium acetylide

[22754-97-8] **C_2Rb_2**



Acids

Mellor, 1946, Vol. 5, 848

With conc. hydrochloric acid ignition occurs, and contact with nitric acid causes explosion.

Halogens

Mellor, 1946, Vol. 5, 848

It burns in all four halogens.

Metal oxides

Mellor, 1946, Vol. 5, 848—850

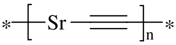
Iron(III) oxide and chromium(III) oxide react exothermally, and lead oxide explosively. Copper oxide and manganese dioxide react at 350°C incandescently.

Non-metal oxides
Mellor, 1946, Vol. 5, 848
Warming in carbon dioxide, nitrogen oxide or sulfur dioxide causes ignition.

Non-metals
Mellor, 1946, Vol. 5, 848
It reacts vigorously with boron or silicon on warming, ignites with arsenic, and burns in sulfur or selenium vapours.
See other METAL ACETYLIDES

1022. Strontium acetylide

[12071-29-3] **$(C_2Sr)_n$**



Halogens
Mellor, 1946, Vol. 5, 862
Strontium acetylide incandesces with chlorine, bromine or iodine at 197, 174 and 182°C, respectively.
See other METAL ACETYLIDES

1023. Thorium dicarbide

[12674-40-7] **C_2Th**

Th^{8+} C^{4-} C^{4-}

Non-metals, or Oxidants
Mellor, 1946, Vol. 5, 862
Contact with selenium or sulfur vapour causes the heated carbide to incandesce. Contact of the carbide with molten potassium chlorate, potassium nitrate or even potassium hydroxide causes incandescence.
See other METAL NON-METALLIDES

1024. Uranium dicarbide

[12071-33-9] **C_2U**

U^{8+} C^{4-} C^{4-}

1. Mellor, 1946, Vol. 5, 890
2. Sidgwick, 1950, 1071

Uranium carbide emits brilliant sparks on impact, ignites on grinding in a mortar [1], or on heating in air to 400°C [2].

Halogens

Mellor, 1946, Vol. 5, 891

Incandesces in warm fluorine, in chlorine at 300°C and weakly in bromine at 390°C.

Hydrogen chloride

See Hydrogen chloride: Metal acetylides or carbides

Nitrogen oxide

See Nitrogen oxide: Metal acetylides or carbides

Water

1. Sidgwick, 1950, 1071
2. Mellor, 1946, Vol. 5, 890—891

Interaction with hot water is violent [1], and the carbide ignites in steam at dull red heat [2].

See other METAL NON-METALLIDES

1025. Zirconium dicarbide

[12070-14-3] **C_2Zr**

$$Zr^{8+} \quad C^{4-} \quad C^{4-}$$

Halogens

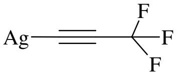
Mellor, 1946, Vol. 5, 885

It ignites in cold fluorine, and in chlorine, bromine and iodine at 250, 300 and 400°C, respectively.

See other METAL NON-METALLIDES

1026. Silver trifluoropropynide

[ ] **C_3AgF_3**



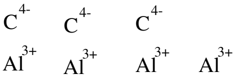
Henne, A. L. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 1042

Explosive decomposition on heating.

See other HALOACETYLENE DERIVATIVES, SILVER COMPOUNDS

1027a. Aluminium carbide

[1299-86-1] **C_3Al_4**



$$\begin{array}{cccc} C^{4-} & C^{4-} & C^{4-} & \\ Al^{3+} & Al^{3+} & Al^{3+} & Al^{3+} \end{array}$$

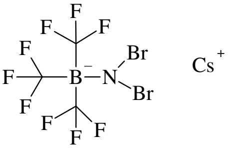
Oxidants

Mellor, 1946, Vol. 5, 872

Incandescence on warming with lead dioxide or potassium permanganate.

See other METAL NON-METALLIDES

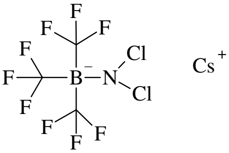
1027b. Caesium *N,N*-Dibromoamino-tris(trifluoromethyl)borate (Cesium (bromimidato)tris(trifluoromethylborate)
[244010-62-6] **$C_3BBr_2CsF_9N$**



Brauer, D. *et al., Inorg. Chem.*, 1999, **38**(18), 3972

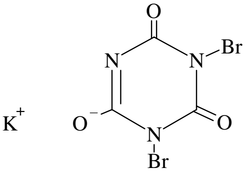
Heating samples of this or the corresponding chlorine compounds, leads to explosions if contaminated with caesium bromate or chlorate, which are byproducts of the syntheses.

1027c. Caesium *N,N*-Dichlorooamino-tris(trifluoromethyl)borate (Cesium (chlormimidato)tris(trifluoromethylborate)
[244010-61-5] **$C_3BCl_2CsF_9N$**



Caesium N,N-Dibromoamino-tris(trifluoromethyl)borate

1028. Potassium 1,3-dibromo-1,3,5-triazine-2,4-dione-6-oxide
[15114-46-2] **$C_3Br_2KN_3O_3$**

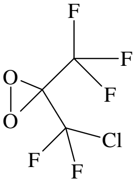


It may be expected to show similar properties to the chloro-analogue.

See Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide

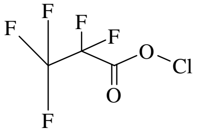
See other *N*-HALOIMIDES

1029. 1-Chlorodifluoromethyl-1-trifluoromethyldioxirane
[35357-48-3] **$C_3ClF_5O_2$**



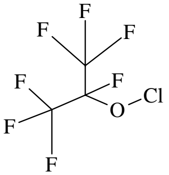
See Bis(trifluoromethyl)dioxirane
See other CYCLIC PEROXIDES

1030. Pentafluoropropionyl hypochlorite
[71359-61-0] **$C_3ClF_5O_2$**



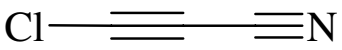
Tari, I. *et al., Inorg. Chem.*, 1979, **18**, 3205—3208
Thermally unstable at 22°C, and explosive in the gas phase at pressures above 27—62 mbar.
See other ACYL HYPOHALITES

1031. Heptafluoroisopropyl hypochlorite
[22675-68-9] **C_3ClF_7O**



Schack. C. J. *et al., J. Amer. Chem. Soc.*, 1969, **91**, 2904
Material condensed at —95°C may suddenly decompose completely and vaporise.
See other HYPOHALITES

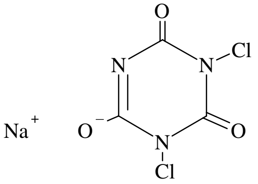
1033. Chlorocyanoacetylene (Chloropropynenitrile)
[2003-31-8] **C_3ClN**



Hashimoto, N. *et al., J. Org. Chem.*, 1970, **35**, 675
Avoid contact with air at elevated temperatures because of its low (unstated) ignition temperature. Burns moderately in the open, but may explode in a nearly closed vessel. Presence of mono- and di-chloroacetylenes as impurities increases the flammability hazard, which may be reduced by addition of 1% of ethyl ether.
See other HALOACETYLENE DERIVATIVES

1034. Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide (Sodium dichloroisocyanurate)

[2893-78-9] [51580-86-0] dihydrate **$C_3Cl_2N_3NaO_3$**



1. 'Fi-Clor 60S', Brochure NH/FS/67.4, Loughborough, Fisons, 1967
2. Paul. J-M. *et al.*, Actualité Chimique, 2004, (274), 10

This compound (sodium dichloroisocyanurate), used in chlorination of swimming pools, is a powerful oxidant and indiscriminate contact with combustible materials must be avoided. Ammonium salts and other nitrogenous materials are incompatible in formulated products [1]. A study of the conditions and mechanisms for conversion of chloroisocyanurates to chloramines has been reported [2]. The dibromo analogue, used for the same purpose, will behave similarly.

See also Ammonium nitrate

Calcium hypochlorite

1. Jones, C., INTERNET: CatJones@FC. KERN.ORG
2. Kirk Othmer, 1998, Vol.25, 592

Although calcium hypochlorite is used in conjunction with sodium dichloroisocyanurate (usually as the dihydrate) for swimming pool maintenance, they must not be mixed undiluted. Noxious fumes and violent explosion or fire can result [1]. Although the organic compound is, at first sight, at its highest oxidation level, it contains disguised ammonia, and nitrogen trichloride may appear on reaction with hypochlorites [2].

See other N-HALOIMIDES

Organic compounds

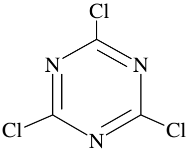
Carpenter, A. R. *et al., Process Safety Progress*, 2003, **22**(2), 75

A formulation of 60% dichloroisocyanurate with 30% of unspecified solid organic material decomposed with vigorous fume emission during the packing of a half-tonne batch. The mixing had been scaled up, via 50 kg pilot trials, only shortly before. It was known, but not realised, that the mix was unstable, showing thermal runaway from 75°C. It is presumed that the blender produced hot-spots from friction, which propagated in the hopper.

Preparative hazard

See 1,3,5-Trichloro-1,3,5-triazinetrione: Cyanuric acid, etc.

1035. 2,4,6-Trichloro-1,3,5-triazine (Cyanuric chloride)
[108-77-0] $C_3Cl_3N_3$



HCS 1980, 925

1. Anon., *Loss Prev. Bull.*, 1979, (025), 21—22
2. *See entry* SELF-ACCELERATING REACTIONS

Of the factors associated with the high reactivity of cyanuric chloride (high exothermicity, rapid hydrolysis in presence of water-containing solvents, acid catalysed reactions, liberation of up to 3 mol hydrogen chloride/mol of chloride, formation of methyl chloride gas with methanol, formation of carbon dioxide from bicarbonates), several were involved in many of the incidents recorded [1] (and given below). The acid catalysed self acceleration and high exothermicity are rated highest [2]. It is also a mildly endothermic compound (ΔH_f° (s) +91.6 kJ/mol, 0.49 kJ/g).

Acetone, Water

Anon., *Loss Prev. Bull.*, 1979, (025), 20

The chloride was to be purified by dissolution in dry acetone, but in error, acetone containing 40% of water was used. The acid-catalysed exothermic hydrolysis reaction of the chloride accelerated to runaway, and gas and vapour evolution ruptured the vessel, leading to fire and explosion.

See Methanol below

See also Water, below

See other GAS EVOLUTION INCIDENTS, SELF-ACCELERATING REACTIONS

Allyl alcohol, Sodium hydroxide, Water

Anon., *Loss Prev. Bull.*, 1974, (001), 11; 1979, (029), 21

When aqueous sodium hydroxide was added to a mixture of the chloride and alcohol at 28°C instead of the normal 5°C, a rapidly accelerating reaction led to rupture of the bursting disc and a gasket, and subsequently to a flash-fire and explosion.

See Methanol below

See also Water, below

2-Butanone, Sodium hydroxide, Water

Anon., *Loss Prev. Bull.*, 1979, (025), 21

The total product of a batch containing a chlorotriazine, water, sodium hydroxide and 2-butanone had not been discharged from the 11,000 l vessel when a further 1.5 t of cyanuric chloride was charged ready for the next batch. The ensuing rapid exothermic hydrolysis led to eruption of the reactor contents, ignition and explosion of butanone vapour, and damage of 3M dollars.

Dimethyl sulfoxide

See Dimethyl sulfoxide: Acyl halides

Dimethylformamide

Anon., *BCISC Quart. Safety Summ.*, 1960, **35**, 24

Cyanuric chloride reacts vigorously and exothermically with DMF after a deceptively long induction period. The 1:1 adduct initially formed decomposes above 60°C with evolution of carbon dioxide and formation of a dimeric unsaturated quaternary ammonium salt. Dimethylformamide is appreciably basic and is not a suitable solvent for acyl halides.

See other INDUCTION PERIOD INCIDENTS

2-Ethoxyethanol

Anon., *Loss Prev. Bull.*, 1979, (025), 20

Alcoholysis of the chloride on the plant scale was effected at 40°C (with brine cooling) by adding portions to the alcohol alternately with finely crystalline disodium phosphate to neutralise the hydrogen chloride produced. On one occasion, use of coarsely crystalline sodium phosphate (of low surface area) reduced the rate of neutralisation, the mixture became acid, and a runaway exotherm to 170°C developed leading to eruption of vessel contents. On another occasion, accidental addition of sodium sulfate instead of phosphate led to a similar situation beginning to develop, but an automatic pH alarm allowed remedial measures to be instituted successfully.

See other NEUTRALISATION INCIDENTS

Methanol

Anon., *ABCM Quart. Safety Summ.*, 1960, **31**, 40

Cyanuric chloride dissolved in methanol reacted violently and uncontrollably with the solvent. This was attributed to the absence of an acid acceptor to prevent the initially acid catalysed (and later auto-catalysed) exothermic reaction of all 3 chlorine atoms simultaneously.

Methanol, Sodium hydrogen carbonate

Anon., *Loss Prev. Bull.*, 1979, (025), 19

A crust of residual cyanuric chloride left in a reactor from a previous batch reacted with the methanol (usually charged first) to form hydrogen chloride. When the base was added (usually before the chloride), vigorous evolution of carbon dioxide expelled some of the solvent. In a second incident, accidentally doubling the charge of cyanuric chloride but not the base, led to the development of free acid (which auto-catalyses the reaction with methanol), and a runaway reaction developed causing violent boiling of the solvent, methyl chloride evolution and damage to the plant.

See Methanol above

See other RUNAWAY REACTIONS

Sodium azide

See 2,4,6-Triazido-1,3,5-triazine (reference 2)

Water

MCA Case History No. 1869

A reaction mixture containing the chloride and water, held in abeyance before processing, developed a high internal pressure in the containing vessel. Hydrolysis (or alcoholysis) of the chloride becomes rapidly exothermic above 30°C.

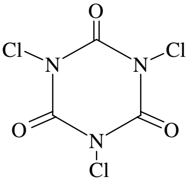
See Allyl alcohol above

See also Methanol, both above

See other ENDOTHERMIC COMPOUNDS

See related ACYL HALIDES

1036. 1,3,5-Trichloro-1,3,5-triazinetrione ('Trichloroisocyanuric acid')
[87-90-1] **$C_3Cl_3N_3O_3$**



HCS 1980, 920

2-(1-Chloroalkyl)-4-methyl-1,3-dioxolanes, Dimethylformamide

Boni, M. *et al., Bull. Chem. Soc. Jap.*, 1994, **67**(6), 1622

This mix is used to oxidise the dioxolane, added all at once to a solution of 28 millimoles of trichloroisocyanuric acid in 16 ml of the solvent. Reaction was explosive above 30°C.

Combustible materials

'Fi-Clor 91' Brochure, Loughborough, Fisons, 1967

This compound, used in chlorination of swimming pools, is a powerful oxidant, and indiscriminate contact with combustible materials must be avoided. The tribromo analogue would be similar.

Cyanuric acid, Sodium hydroxide

Brennan, J. P., US Pat. 4 118 570, 1978

Formation of sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide ('sodium dichloroisocyanurate') from an aqueous slurry of the trione, cyanuric acid and sodium hydroxide is accompanied by evolution of nitrogen trichloride. Nitrogen purging will keep the concentration of the explosive gas below the lower explosive limit of 5—6%.

Water

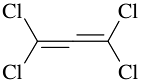
1. Young, J. A., private comm., 1986
2. Paul, J-M. *et al., Actualité Chimique*, 2004, (274), 10

If mixed with a small amount of water, the conc. Solution (with pH around 2) may explode, owing to evolution of nitrogen trichloride. It is believed that hydrolysis leads to formation of hypochlorous acid and dichloro-*s*-triazinetrione, and the protonated acid then attacks the C=N bonds in the triazine ring leading to formation of chloramines and nitrogen trichloride. The dichloro compound is stable to acid in absence of hypochlorous acid [1]. A study of the exact conditions and mechanism of conversion of chloroisocyanurates to chloramines, with or without added ammonium ions, is reported [2].

See other N-HALOIMIDES

1038. Tetrachloropropadiene

[18608-30-5] **C_3Cl_4**



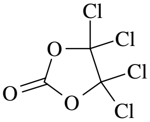
Tetracarbonylnickel

See Dicarbonyl-η-trichloropropenyldinickel chloride dimer

See other HALOALKENES

1039a. Tetrachloroethylene carbonate

[22432-68-4] **$C_3Cl_4O_3$**



Tributylamine

1. Fagenburg, D. R., *Chem. Eng. News*, 1982, **60**(33), 45
2. Melby, L. R., *Chem. Eng. News*, 1982, **60**(40), 2

Interaction of the two compounds led to the evolution of a toxic gas thought to be chlorine [1]. It is the far more poisonous phosgene, arising from the known base-catalysed disproportionation of the carbonate to oxalyl chloride and phosgene, which occurs even at ambient temperature [2]. (The editor knows that amides, too, catalyse this rearrangement and suspects that Lewis acids will also)

See other GAS EVOLUTION INCIDENTS

1039b. Trichloromethyl carbonate (Triphosgene)

[32315-10-9] **$C_3Cl_6O_3$**

$(CCl_3O)_2CO$

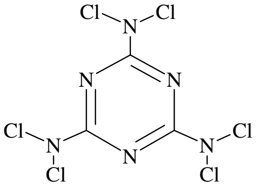
1. Hollingsworth, M. D., *Chem. Eng. News*, 1993, **70**(28), 2
2. McDonald, R., *Chem. Eng. News*, 2001, **79**(5), 7

A package of this, consisting of a wax-coated glass jar in vermiculite within a sealed can, was found to be pressurised when opened. The cap of the jar had cracked, and it was assumed that residual water on the vermiculite had reacted to form hydrogen chloride, phosgene and carbon dioxide. Similar mishaps had been experienced elsewhere. Less packing would have given rise to less danger; the supplier has, however, supplemented the four layers initially present with a fifth and a recommendation not to store long and then under refrigeration [1]. (The editor would predict that there are possible contaminants which could rearrange this compound slowly to phosgene in absence of water). A manufacturer agrees that there are numerous impurities – including metal ions, nucleophiles and charcoal – which can catalyse the slow decomposition of triphosgene to gaseous products, including phosgene. Properly purified, packed and stored it remains a valuable and safe reagent [2].

See other PACKAGING INCIDENTS

1040. 2,4,6-Tris(dichloroamino)-1,3,5-triazine (Hexachloromelamine)

[2428-04-8] **$C_3Cl_6N_6$**



As a trifunctional dichloroamino compound, it is probably more reactive and less stable than the monochloroamino analogue.

Acetone, or Bases

491M, 1975, 197

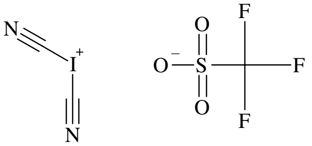
Addition of acetone, ammonia, aniline or diphenylamine to the oxidant causes rapid exothermic reactions, with or without flame, and large amounts under confinement would explode. The trichloro analogue is similar, but less vigorous.

See 2,4,6-Tris(chloroamino)-1,3,5-triazine (next above)

See other *N*-HALOGEN COMPOUNDS

1041. Potassium tricyanodiperoxochromate(3—)

[65521-60-0] **$C_3CrK_3N_3O_4$**



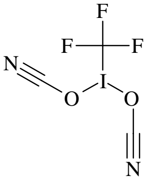
Bailar, 1973, Vol. 4, 167

A highly explosive material, with internal redox features.

See other PEROXOACID SALTS, REDOX COMPOUNDS

1042. Trifluoromethyliodine(III) isocyanate

[127510-65-0] **$C_3F_3IN_2O_2$**



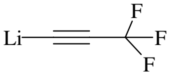
Naumann, D. *et al., J. Fluor. Chem.*, 1989, **45**(3), 401

This compound explosively decomposes when warmed up to room temperature.

See other IODINE COMPOUNDS, ORGANIC ISOCYANATES

1043. Lithium trifluoropropynide

[14856-86-1] **C_3F_3Li**

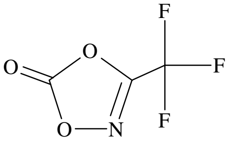


See Lithium chloroacetylide

See other HALOACETYLENE DERIVATIVES, METAL ACETYLIDES

1044. 2-Trifluoroacetyl-1,3,4-dioxazalone

[87050-94-0] **$C_3F_3NO_3$**



Middleton, W. J., *J. Org. Chem.*, 1983, **48**, 3845

A sample contained in a dropping funnel at 25°C exploded forcefully. Though not sensitive to mechanical shock, it could be detonated by a hot wire when unconfined, or if rapidly heated to 220°C when confined in a stainless steel capillary.

See 1,3,4-DIOXAZOLONES

1045. Dicyanoiodonium triflate

[ ] **$C_3F_3IN_2O_3S$**

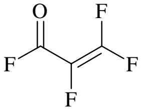
$(NC)_2I^+ \ CF_3SO_3^-$

Steng, P. J. *et al., Tetrahedron Lett.*, 1992, **33**(11), 1419

This iodinating reagent is storable under nitrogen at —20°C; it may explode after contact with air. It decomposes in minutes at ambient temperatures.

See other CYANO COMPOUNDS, IODINE COMPOUNDS

1046. Trifluoroacryloyl fluoride
[667-49-2] **C_3F_4O**



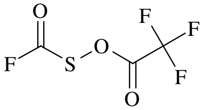
Sodium azide

Middleton, W. J., *J. Org. Chem.*, 1973, **38**, 3294

The product of interaction was an unidentified highly explosive solid.

See other ACYL HALIDES

1047. *O*-Trifluoroacetyl-*S*-fluoroformyl thioperoxide
[27961-70-2] **$C_3F_4O_3S$**

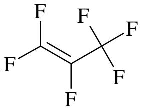


Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 378

It exploded spontaneously in a glass bomb closed with a PTFE-lined valve. No previous indications of instability had been noted during distillation, pyrolysis or irradiation.

See related DIACYL PEROXIDES

†1048. Hexafluoropropene
[116-15-4] **C_3F_6**



Air, Tetrafluoroethylene

See Tetrafluoroethylene: Air, Hexafluoropropene

Grignard reagents

Dinowski, W., *J. Fluorine Chem.*, 1981, **18**, 25—30

Reaction of various substituted phenylmagnesium bromides with hexafluoropropene under pressure at ambient temperature had been effected on the 0.2—0.6 g mol scale without incident. An attempt to scale up to 0.8 g mol with phenylmagnesium bromide led to an explosion.

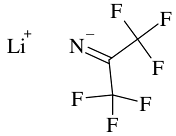
Oxygen, Oxygen difluoride

See Oxygen difluoride: Hexafluoropropene, etc.

See other HALOALKENES

1049. Hexafluoroisopropylideneaminolithium

[31340-36-0] **C_3F_6LiN**



Non-metal halides

Swindell, R. F., *Inorg. Chem.*, 1972, **11**, 242

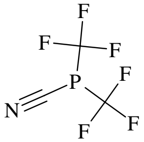
Interaction of the lithium derivative with a range of chloro- and fluoro-derivatives of arsenic, boron, phosphorus, silicon and sulfur during warming to 25°C tended to be violently exothermic in absence of solvent. Thionyl chloride reacted with explosion.

See Hexafluoroisopropylideneamine: Butyllithium

See other N-METAL DERIVATIVES

1050. Bis(trifluoromethyl)cyanophosphine

[431-97-0] **C_3F_6NP**



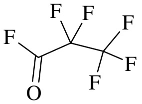
491M, 1975, 60

It ignites in air.

See related ALKYLHALOPHOSPHINES, CYANO COMPOUNDS

1051. Pentafluoropropionyl fluoride

[422-61-7] **C_3F_6O**



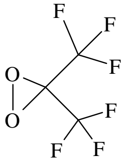
Fluorinated catalysts

Sorbe, 1968, 2

The acid fluoride may decompose explosively in contact with fluorinated catalysts.

See other ACYL HALIDES

1052. Bis(trifluoromethyl)dioxirane
[35357-46-1] **$C_3F_6O_2$**

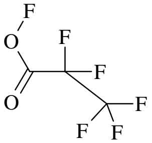


Ando, W. (Ed.), *Organic Peroxides*, 195, Wiley, New York, 1992.

Formed by fluorine oxidation of the dilithium salt of hexafluoroacetone hydrate, it is unstable and explosive. The chloropentafluoro homologue is similar. Proponents of their use as reagents claim that the dimethyl and methyltrifluoromethyl analogues are not explosive; this seems improbable, especially since the less stressed lower dioxetanes (homodioxiranes) are all dangerous.

See other CYCLIC PEROXIDES

1053. Pentafluoropropionyl hypofluorite
[ ] **$C_3F_6O_2$**



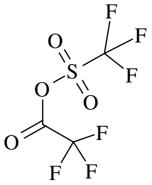
Menefee, A. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 2020

Less stable than its lower homologue, the hypofluorite explodes on sparking, on distillation at ambient pressure (b.p., 2°C), though not at below 0.13 bar.

See Fluorine: Caesium heptafluoropropoxide

See other ACYL HYPOHALITES

1054. Trifluoroacetyl trifluoromethanesulfonate
[68602-57-3] **$C_3F_6O_4S$**



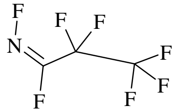
Forbus, T. R. *et al., J. Org. Chem.*, 1979, **44**, 313

The mixed anhydride reacts almost explosively with water.

See other ACID ANHYDRIDES, SULFUR ESTERS

1055. 1-Fluoroiminohexafluoropropane

[78343-32-5] **C_3F_7N**



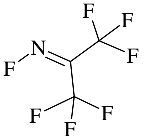
Fluorine

See Fluorine: 1- or 2-Fluoroiminohexafluoropropane

See other *N*-HALOGEN COMPOUNDS

1056. 2-Fluoroiminohexafluoropropane

[2802-70-2] **C_3F_7N**



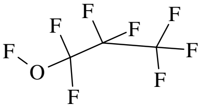
Fluorine

See Fluorine: 1- or 2-Fluoroiminohexafluoropropane

See other *N*-HALOGEN COMPOUNDS

1057. Heptafluoropropyl hypofluorite

[2203-57-8] **C_3F_8O**



1. Sorbe, 1968, 62
2. *MCA Case History No. 1045*

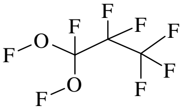
An explosive compound [1], and the preparation is hazardous, involving the fluorination of caesium perfluoropropoxide [2].

See Fluorine: Caesium heptafluoropropoxide

See other HYPOHALITES

1058. 1,1-Bis(fluorooxy)hexafluoropropane

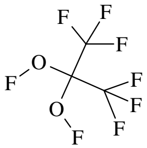
[72985-54-7] **$C_3F_8O_2$**



Explosive, less stable than its lower homologue.
See entry BIS(FLUOROOXY)PERHALOALKANES

1059. 2,2-Bis(fluorooxy)hexafluoropropane (2,2,2-Trifluoro-1-(trifluoromethyl) ethylidene dihypofluorite)

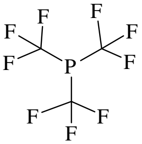
[16329-93-4] **$C_3F_8O_2$**



Zedda, A. *et al., Inorg. Chem.*, 1995, **34**(22), 5686
It is especially prone to explosive decomposition. Use at vapour pressures above 30 mBar is not advised. It is a strong oxidiser. An improved preparation is described.
See entry BIS(FLUOROOXY)PERHALOALKANES
See other HYPOHALITES

1060. Tris(trifluoromethyl)phosphine

[432-04-2] **C_3F_9P**



Oxygen
Mahler, W., *Inorg. Chem.*, 1979, **18**, 352
Contact with oxygen at 25°C/0.5 bar causes ignition of the phosphine.
See related ALKYLPHOSPHINES

1061. Sodium tricarbonylnitrosylferrate

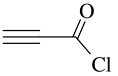
[25875-18-7] **$C_3FeNNaO_4$**

$[(CO)_3FeNO]^-Na^+$

Davies, S. G. *et al., J. Organomet. Chem.*, 1990, **386**(2), 195
This compound is air sensitive and decomposes explosively. Use of the more stable tetrabutylammonium salt as a reagent for carbonylation of alkyl halides is recommended.

1062a. Propioloyl chloride (Propynoyl chloride)

[50277-65-1] **C_3HClO**



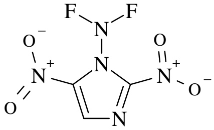
Balfour, W. J. *et al., J. Org. Chem.*, 1974, **39**, 726

This chloride, purified by distillation at 58—60°C/1 bar usually ignites spontaneously in air owing to presence of chloroacetylene (formed by decarbonylation), but vacuum distillation at cryogenic temperatures prevents formation of the impurity.

See other ACETYLENIC COMPOUNDS, ACYL HALIDES

1062b. 1-(Difluoroamino)-2,4-dinitroimidazole

[175788-63-3] **$C_3HF_2N_5O_4$**



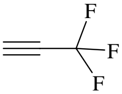
Dalinger, I. L. *et al., Mendeleev Comm.* 1996, (1), 13

Advanced as the type of a new series of difluorohydrazines, it is shock sensitive.

See other DIFLUOROAMINO COMPOUNDS

1063. 3,3,3-Trifluoropropyne

[661-54-1] **C_3HF_3**



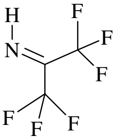
Haszeldine, R. N., *J. Chem. Soc.*, 1951, 590

It tends to explode during analytical combustion, and the copper(I) and silver derivatives decomposed violently (with occasional explosion) on rapid heating.

See other HALOACETYLENE DERIVATIVES

1064. Hexafluoroisopropylideneamine (2-Iminohexafluoropropane)

[1645-75-6] **C_3HF_6N**



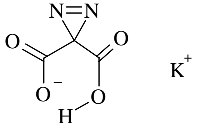
Butyllithium

Swindell, R. F. *et al., Inorg. Chem.*, 1972, **11**, 242

The exothermic reaction which set in on warming the reagents in hexane to 0°C sometimes exploded if concentrated solutions of butyllithium (above 2.5 M) were used, but not if diluted (to about 1.2 M) with pentane.

1065. Potassium hydrogen diazirine-3,3-dicarboxylate

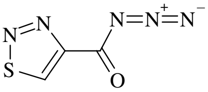
[ ] **$C_3HKN_2O_4$**



See Diazirine-3,3-dicarboxylic acid
See other DIAZIRINES

1066. 4-Azidocarbonyl-1,2,3-thiadiazole

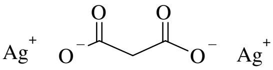
[ ] **C_3HN_5OS**



Pain, D. L. *et al. J. Chem. Soc.*, 1965, 5167
The azide is extremely explosive in the dry state, though the oxygen balance is —54%.
See OXYGEN BALANCE
See other ACYL AZIDES

1068a. Silver malonate

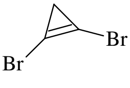
[57421-56-4] **$C_3H_2Ag_2O_4$**



Sorbe, 1968, 126
It explodes on heating.
See other SILVER COMPOUNDS

1068b. 1.2-Dibromocyclopropene

[108186-05-6] **$C_3H_2Br_2$**



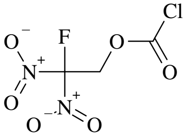
Baird, M. S. *et al., Tetrahedron Lett.*, 1995, **36**(19), 3393

This highly strained compound decomposes violently even at room temperature; handle with great care.

See other STRAINED-RING COMPOUNDS

1069. 2,2-Dinitro-2-fluoroethoxycarbonyl chloride

[31841-79-9] **$C_3H_2ClFN_2O_6$**



Potassium picrate

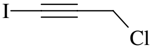
Becuwe, A. G. *et al.*, US Pat. 4 145 361, 1979

Interaction to give the (explosive) ester, 2,2-dinitro-2-fluoroethyl 2,4,6-trinitrophenyl carbonate must be effected at below 50°C to prevent explosion.

See other ACYL HALIDES, FLUORODINITROMETHYL COMPOUNDS

1070. 3-Chloro-1-iodopropyne

[109-71-7] **C_3H_2ClI**



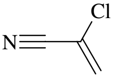
Houben-Weyl, 1977, Vol. 5.2a, 610

Distillation at 47°C/5 mbar should only be taken to a 33% residue; less may lead to violent decomposition, as may admission of air to the hot residue.

See other HALOACETYLENE DERIVATIVES

†1071. 2-Chloroacrylonitrile

[920-37-6] **C_3H_2ClN**

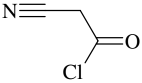


See other CYANO COMPOUNDS

See related HALOALKENES

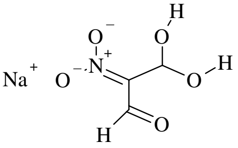
1072. Cyanoacetyl chloride

[16130-58-8] **C_3H_2ClNO**



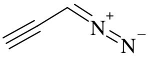
491M, 1975, 140
After treating cyanoacetic acid with phosphorus pentachloride, volatile materials were distilled off and the crude chloride was left in a stoppered flask. After 24 h the flask exploded.
See other ACYL HALIDES, CYANO COMPOUNDS

1073a. Sodium diformylnitromethanide hydrate
[34461-00-2] **$C_3H_2NNaO_4.H_2O$**



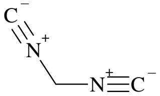
Fanta, P. E., *Org. Synth.*, 1962, Coll. Vol. 4, 844
The monohydrate, possibly the *gem*-dihydroxy compound and an *aci*-nitro salt, is an impact-sensitive solid and must be carefully handled with precautions.
See related aci-NITRO SALTS, C—NITRO COMPOUNDS

1073b. Diazopropyne
[17761-23-8] **$C_3H_2N_2$**



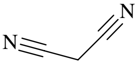
Wierlacher, S. *et al., Chem. Phys. Lett.*, 1994, **222**(4), 319
This compound is highly explosive and has detonated violently when in use on laboratory scale.
See other ACETYLENIC COMPOUNDS, DIAZO COMPOUNDS

1074. Diisocyanomethane
[92-79-7] **$C_3H_2N_2$**



Buschmann, J. *et al., Angew. Chem. (Int.)*, 1997, **36**(21), 2372
A clear crystalline solid at —55°C, this compound melts, with browning at —15°C, and decomposes explosively at —10°C, leaving a polymer.
See other DIISOCYANIDE LIGANDS

1075. Malononitrile (Propanedinitrile)
[109-77-3] **$C_3H_2N_2$**



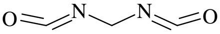
Severely endothermic: ΔH_f° 186 kJ/mole, 2.8 kJ/g. Energy of decomposition (in range 180—270°C) measured as 1.65 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ENDOTHERMIC COMPOUNDS

Alone, or Bases

1. Personal experience
2. 'Malononitrile' Brochure, p. 11, Basle, Lonza Ltd., 1974
3. Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 29

It may polymerise violently on heating at 130°C, or in contact with strong bases at lower temperatures [1]. The stability of the molten nitrile decreases with increasing temperature and decreasing purity, but no violent decomposition below 100°C has been recorded [2]. However, a partially filled drum of malononitrile stored in an oven at 70—80°C for 2 months exploded violently [3].
See other CYANO COMPOUNDS

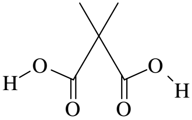
1076. Diisocyanatomethane (Methylene diisocyanate)
[4747-90-4] **$C_3H_2N_2O_2$**



Dimethylformamide

'DMF Chemical Uses', Brochure, Wilmington, Du Pont, 1967
Contact with the basic solvent causes violent polymerisation of the isocyanate.
See other POLYMERISATION INCIDENTS
See related CYANO COMPOUNDS

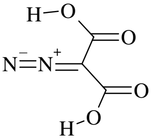
1077. Diazirine-3,3-dicarboxylic acid
[76429-98-6] **$C_3H_2N_2O_4$**



Schustov, G. V. *et al., Angew. Chem. (Intern. Ed.)*, 1981, **20**, 200
While the dipotassium salt is stable for over 2 months at 20°C, the monopotassium salt exploded within a few hours at 0°C. Both salts exploded when triturated.
See other DIAZIRINES, ORGANIC ACIDS

1078. Diazomalonic acid

[59348-62-8] **$C_3H_2N_2O_4$**



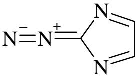
1. *491M*, 1975, 144
2. *DOC 5*, 1982, 1588

During attempted distillation of the impure acid at 4 mbar, the (involatile) sample exploded [1]. The free acid is unknown, but the diethyl ester has exploded during low pressure distillation [2].

See other DIAZO COMPOUNDS, ORGANIC ACIDS

1079. 2-Diazo-2H-imidazole

[50846-98-5] **$C_3H_2N_4$**



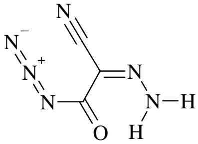
As an isolated solid, the compound is shock-sensitive and should be freshly prepared only as a solution for immediate use.

See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS

1080. Cyanohydrazonoacetyl azide

[115057-44-8] **$C_3H_2N_6O$**



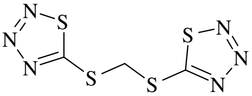
Kobolov, M. Yu. *et al., Chem. Abs.*, 1988, **109**, 20908

It explodes on melting.

See other ACYL AZIDES, CYANO COMPOUNDS, HIGH-NITROGEN COMPOUNDS

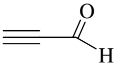
1081. Bis(1,2,3,4-thiatriazol-5-ylthio)methane

[ ] **$C_3H_2N_6S_4$**



Pilgram, K. *et al., Angew. Chem.*, 1965, **77**, 348
This compound (which is 'sulfur balanced'), and its three longer chain homologues, explodes loudly with a flash on impact, or on heating to the m.p.
See OXYGEN BALANCE
See other N—S COMPOUNDS

1082. Propiolaldehyde (Propynal)
[624-67-9] **C_3H_2O**

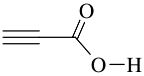


Bases

1. Sauer, J. C., *Org. Synth.*, 1963, Coll. Vol. 4, 814
2. Makula, D. *et al., L'Actual. Chim.*, 1983, (6), 31—34

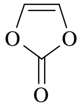
The acetylenic aldehyde undergoes vigorous polymerisation in presence of alkalies and, with pyridine, the reaction is almost explosive [1]. The ground glass stopper of a 1 l brown bottle containing 750 ml of the aldehyde in toluene (2:1) and stored for 8 years was found to be seized. During attempts to open it an explosion occurred, leaving 250 ml of a polymeric residue in the bottle. DSC experiments and modeling calculations led to the conclusion that polymerisation had been initiated at ambient temperature by flakes of (alkaline) soda glass and peroxidic material (which had seized the stopper) falling into the solution of aldehyde. It is recommended that propynal should not be stored in glass, and only as a dilute (10%) solution [2] and for strictly limited periods.
See Acrylaldehyde
See other ACETYLENIC COMPOUNDS, ALDEHYDES, GLASS INCIDENTS, POLYMERISATION INCIDENTS

1083. Propiolic acid (Propynoic acid)
[471-25-0] **$C_3H_2O_2$**



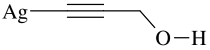
Ammonia, Heavy metal salts
Baudrowski, E., *Ber.*, 1882, **15**, 2701
Interaction of the acid with ammoniacal solutions of copper(I) or silver salts gives precipitates which explode on warming or impact. The structures are not given, but may be amminemetal acetylide salts.
See METAL ACETYLIDES
See other ACETYLENIC COMPOUNDS, ORGANIC ACIDS

1084. 1,3-Dioxol-4-en-2-one (Vinylene carbonate)
[872-36-6] **$C_3H_2O_3$**



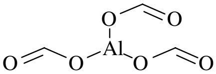
Archer, M., private comm., 1979
A 7 year old screw capped sample burst in storage. Peroxide formation seems a less likely cause than slow hydrolysis and carbon dioxide evolution, though both are possibilities.
See related GAS EVOLUTION INCIDENTS, PEROXIDISABLE COMPOUNDS

1085. Silver 3-hydroxypropynide
[ ] **C_3H_3AgO**



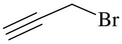
Karrer, P., Organic Chemistry, 111, London, Elsevier, 4th Engl. Edn., 1950
The silver salt is explosive.
See other METAL ACETYLIDES, SILVER COMPOUNDS

1086. Aluminium formate
[7360-53-4] **$C_3H_3AlO_6$**



Anon., *ABCM Quart. Safety Summ.*, 1939, **10**, 1
An aqueous solution of aluminium formate was being evaporated over a low flame. When the surface crust was disturbed, an explosion occurred. This seems likely to have been due to thermal decomposition of the solid, liberation of carbon monoxide and ignition of the latter admixed with air.

†1087. 3-Bromopropyne (Propargyl bromide)
[106-96-7] **C_3H_3Br**



HCS 1980, 784, (785 in toluene)

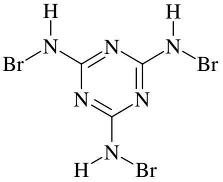
1. Coffee, R. D. *et al., Loss Prev.*, 1967, **1**, 6—9
2. Driedger, P. E. *et al., Chem. Eng. News*, 1972, **50**(12), 51
3. Brown, J. P,. 1991, personal communication
4. Forshey, *Fire Technol.*, 1969, **5**, 100—111

This liquid acetylenic endothermic compound (ΔH_f° estimated as 230—270 kJ/mol, ~2 kJ/g) may be decomposed by mild shock, and when heated under confinement, it decomposes with explosive violence and may detonate. Addition of 20—30 wt% of toluene makes the bromide insensitive in laboratory impact and confinement tests [1]. More recently, it was classed as extremely shock-sensitive [2]. It can be ignited by impact derived from the 'liquid-hammer' effect of accidental pressurisation of the aerated liquid, and will then undergo sustained (monopropellant) burning decomposition. Propargyl bromide, added dropwise to bromine, exploded as it neared the halogen [3]. The chloro analogue is similar, but less readily ignited [4].
See other ENDOTHERMIC COMPOUNDS

Metals
Dangerous Substances, 1972, Sect. 1, 27
There is a danger of explosion in contact with copper, high-copper alloys, mercury or silver (arising from metal acetylide formation).
See METAL ACETYLIDES

Trichloronitromethane
See Trichloronitromethane: 3-Bromopropyne
See other HALOACETYLENE DERIVATIVES

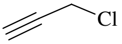
1088. 2,4,6-Tris(bromoamino)-1,3,5-triazine (Tribromomelamine)
[22755-34-6] **$C_3H_3Br_3N_6$**



Vona, J. A. *et al., Chem. Eng. News*, 1952, **30**, 1916
Bromination with this and similar *N*-halogen compounds may become violent or explosive after an induction period as long as 15 min. Small scale preliminary experiments, designed to avoid the initial presence of excess brominating agent, are recommended.
See other INDUCTION PERIOD INCIDENTS

Allyl alcohol
Vona, J. A. *et al., Chem. Eng. News*, 1952, **30**, 1916
The components reacted violently 15 min after mixing at ambient temperature. This seems likely to have been a radical-initiated polymerisation of the alcohol (possibly peroxidised) in absence of diluent.
See other *N*-HALOGEN COMPOUNDS

†1089. 3-Chloropropyne (Propargyl chloride)
[624-65-7] C_3H_3Cl



HCS 1980, 786 (787 in toluene)

Doyle, W. H., *Loss Prev.*, 1969, **3**, 15
Pumping the liquid against a closed valve caused the pump to explode, which detonated the contents of the reservoir tank-car.

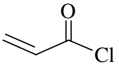
Ammonia

Anon., *Sichere Chemiearb.*, 1956, **8**(6), 45
Interaction of 3-chloropropyne and liquid ammonia under pressure in a static steel bomb had been used several times to prepare the amine. On one occasion the usual slow exothermic reaction did not occur, and the bomb was shaken mechanically. The increased reaction rate led to a rapid exothermic reaction, followed by an explosion. Other cases of instability in propyne derivatives are known.
See 3-Propynol, and 3-Propynethiol
See other AMINATION INCIDENTS

Chlorine

See Chlorine: 3-Chloropropyne
See other HALOACETYLENE DERIVATIVES

†1090. Acryloyl chloride (2-Propenoyl chloride)
[814-68-6] C_3H_3ClO



1. Pyriadi, T. M., *Chem. Eng. News*, 1985, **63**(44), 4
2. Griffith, T. E., *Chem. Eng. News*, 1985, **63**(50), 2
3. Author's comment, 1986

A 500 ml bottle of the acid chloride stabilised with 0.05% of phenothiazine was shipped to a hot climate without refrigeration, and was stored on arrival in a fume cupboard for 2 days at temperatures approaching 50°C. The material polymerised, bursting the bottle and forming a solid foam [1]. The label recommended storage at 4°C. Another manufacturer proposed mislabeling or contamination by moisture to explain the incident [2], but the presence of polymeric foam appears to confirm that polymerisation at the extremely high ambient storage temperature was the primary cause, perhaps with some thermal decomposition and evolution of hydrogen chloride assisting in foam formation [3].
See other ACYL HALIDES, POLYMERISATION INCIDENTS

1091. 1,3-Dithiolium perchlorate

[3706-77-2] **$C_3H_3ClO_4S_2$**

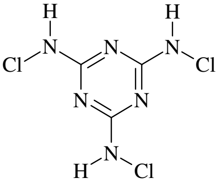
1. Ferraris, J. P. *et al., Chem. Eng. News*, 1974, **52**(37), 3
2. Klingsberg, E., *J. Amer. Chem. Soc.*, 1964, **86**, 5292
3. Leaver, D. *et al., J. Chem. Soc.*, 1962, 5109
4. Wudl, F. *et al., J. Org. Chem.*, 1974, **39**, 3608—3609; *Inorg. Chem.*, 1979, **19**, 28—29
5. Melby, L. R. *et al., J. Org. Chem.*, 1974, **39**, 2456

The salt (an intermediate in the preparation of 1,4,5,8-tetrahydro-1,4,5,8-tetrathiafulvalene) exploded violently during removal from a glass frit with a Teflon-clad spatula [1]. Previous references to the salt exploding at 250°C [2] or melting at 264°C [3] had been made. Use of a salt alternative to the perchlorate is urged [1]. Safer methods suitable for small-scale [4] and large-scale [5] preparations have been described.

See other NON-METAL PERCHLORATES

1092. 2,4,6-Tris(chloroamino)-1,3,5-triazine (Trichloromelamine)

[7673-09-8] **$C_3H_3Cl_3N_6$**



Acetone, or Bases

491M, 1975, 197

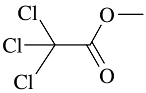
Addition of acetone, ammonia, aniline or diphenylamine to the oxidant causes, after a few seconds delay, a rapid reaction accompanied by smoke and flame.

See 2,4,6-Tris(bromoamino)-1,3,5-triazine

See other N-HALOGEN COMPOUNDS

1093. Methyl trichloroacetate

[598-99-2] **$C_3H_3Cl_3O_2$**



Trimethylamine

Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 197

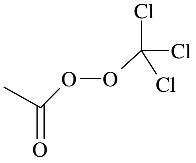
A stirred uncooled mixture in an autoclave reacted violently, the pressure developed exceeding 400 bar. Polymerisation of a reactive species produced by dehydrochlorination of the ester or a decomposition product seems a posibility.

See Sodium hydride: Ethyl 2,2,3-trifluoropropionate

See other POLYMERISATION INCIDENTS

1094. Trichloromethyl peroxyacetate

[94089-34-6] **$C_3H_3Cl_3O_3$**



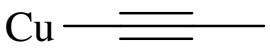
Turner, W. V. *et al., J. Org. Chem.*, 1992, **57**(5), 1610

This compound has caused several explosions in the author's laboratory.

See other PEROXYESTERS

1095. 1-Propynylcopper(I)

[30645-13-7] **C_3H_3Cu**



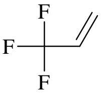
Houben-Weyl, 1977, Vol. 5.2a, 570

Preparation and use of this very explosive compound are detailed.

See other METAL ACETYLIDES

†1096. 3,3,3-Trifluoropropene

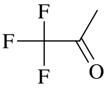
[677-21-4] **$C_3H_3F_3$**



See other HALOALKENES

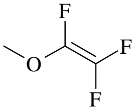
†1097. 1,1,1-Trifluoroacetone

[421-50-1] **$C_3H_3F_3O$**



1098. Methyl trifluorovinyl ether

[3823-94-7] **$C_3H_3F_3O$**



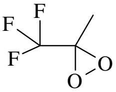
1. Dixon, S., US Pat. 2 917 548, 1959
2. Anderson, A. W., *Chem. Eng. News*, 1976, **54**(16), 5
3. O'Neill, G. J., US Pat. 4 127 613, 1978

Methyl trifluorovinyl ether, b.p. 10.5—12.5°C, prepared from tetrafluoroethylene and sodium methoxide [1], has considerable explosive potential. On ignition, it decomposes more violently than acetylene and should be treated with extreme caution [2]. Other trifluorovinyl ethers are similarly available from higher alkoxides [1], and although not tested for instability, should be handled carefully. Presence of fluorohaloalkanes boiling lower than the ether stabilises the latter against spark-initiated decomposition in both fluid phases [3].

See related HALOALKENES

1099. Methyltrifluoromethyldioxirane

[115464-59-0] **$C_3H_3F_3O_2$**



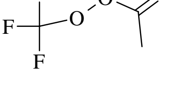
Bis(trifluoromethyl)dioxirane

See Dimethyldioxirane

See other CYCLIC PEROXIDES

1100. Trifluoromethyl peroxyacetate

[33017-08-2] **$C_3H_3F_3O_3$**

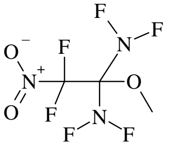


Bernstein, P. A. *et al., J. Amer. Chem. Soc.*, 1971, **93**, 3885

A 1 g sample cooled to —196°C exploded violently when warmed in a bath at 22°C.

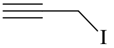
See other PEROXYESTERS

1101. 1,1-Bis(difluoroamino)-2,2-difluoro-2-nitroethyl methyl ether
[30957-47-2] **$C_3H_3F_6N_3O_3$**



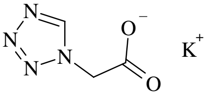
Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3096—3098
A shock-sensitive explosive.
See other DIFLUOROAMINO COMPOUNDS

1102. 3-Iodopropyne
[659-86-9] **C_3H_3I**



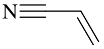
Whiting, M. C., *Chem. Eng. News*, 1972, **50**(23), 86—87
It explodes during distillation at 180°C.
See other HALOACETYLENE DERIVATIVES

1103. Potassium 1-tetrazolacetate
[51286-83-0] **$C_3H_3KN_4O_2$**



Eizember, R. F. *et al., J. Org. Chem.*, 1974, **39**, 1792—1793
During oven-drying, kg quantities of the salt exploded violently. Investigation showed that self-propagating and extremely rapid decomposition of a cold sample can be initiated by local heating to over 200°C by a flint spark, prolonged static spark or flame. The sodium salt could only be initiated by flame, and the free acid is much less sensitive.
See other TETRAZOLES

†1104. Acrylonitrile (Propenenitrile) (Cyanopropene) (Vinyl cyanide)
[107-13-1] **C_3H_3N**



(*MCA SD-31*, 1964); *FPA H51*, 1976; *HCS 1980*, 116; *RSC Lab. Hazards Data Sheet No. 48*, 1986

1. *MCA SD-31*, 1964
2. Harmon, 1974, 2.3

3. Taylor, B. J., *Univ. Safety Assoc. Safety News*, 1972, (1), 5—6
4. Bond, J., *Loss Prev. Bull.*, 1985, (065), 26
5. Wakakura, M. *et al., J. Loss Prev. Process Ind.*, 1999, **12**, 84
6. Personal experience (PGU)

Significantly endothermic: ΔH_f° (l) 147 kJ/mole 2.8 kJ/g. The monomer is sensitive to light, and even when inhibited (with aqueous ammonia) it will polymerise exothermally at above 200°C [1]. It must never be stored uninhibited, or adjacent to acids or bases [2]. Polymerisation of the monomer in a sealed tube in an oil bath at 110°C led to a violent explosion. It was calculated that the critical condition for runaway thermal explosion was exceeded by a factor of 15 [3]. Runaway polymerisation in a distillation column led to an explosion and fire [4]. Another loss of containment and fire resulted from acrylonitrile polymerisation in a waste solvent tank also containing toluene and peroxides (peroxides are polymerisation initiators) [5]. Use of the nitrile as a reagent in synthesis can lead to condensation of its vapour in unseen parts of the equipment, such as vent-pipes and valves, which may then be obstructed or blocked by polymer [6].

See other ENDOTHERMIC COMPOUNDS, POLYMERISATION INCIDENTS

Acids — MRH Nitric acid 6.32/78, sulfuric acid 2.26/48

1. 'Acrylonitrile', London, British Hydrocarbon Chemicals Ltd., 1965
2. Kaszuba, F. J., *J. Amer. Chem. Soc.*, 1945, **67**, 1227
3. Shirley, D. A., *Preparation of Organic Intermediates*, 3, New York, Wiley, 1951
4. Kaszuba, F. J., *Chem. Eng. News*, 1952, **30**, 824
5. Anon., *Loss Prev. Bull.*, 1978, (024), 167
6. Bond, J., *Loss Prev. Bull.*, 1985, (065), 26

Contact of strong acids (nitric or sulfuric) with acrylonitrile may lead to vigorous reactions. Even small amounts of acid are potentially dangerous, as these may neutralise the aqueous ammonia present as polymerisation inhibitor and leave the nitrile unstabilised [1]. Precautions necessary in the hydrolysis of acrylonitrile [2] are omitted in the later version of the procedure [3]. It is essential to use well-chilled materials (acrylonitrile, diluted sulfuric acid, hydroquinone, copper powder) to avoid eruption and carbonisation. A really wide-bore condenser is necessary to contain the vigorous boiling of unhydrolysed nitrile [4]. Leaking valves or operator error caused contamination of a 1000 l dosing vessel of the nitrile with conc. sulfuric acid, and an explosion ensued [5]. Contamination of a drum of acrylonitrile by nitric acid residues in the filling hose led to a slowly accelerating polymerisation reaction which burst the drum after 10 days [6].

See Bromine, etc., below

Bases — MRH Potassium or sodium hydroxides 2.84/tr.

1. *MCA SD-31*, 1964
2. Castaneda Hernandez, H. R. *et al., Chem. Abs.*, 1987, **107**, 78274

Acrylonitrile polymerises violently in contact with strong bases, whether stabilised or unstabilised [1]. Alkaline hydrolysis of acrylonitrile is exothermic and violent, especially when the temperature is above 60°C, the pressure is above atmospheric, and when heating at 60°C is prolonged above 10 mins. Polymerisation does not induce a violent reaction at 40—50°C at a concentration of 3% of sodium hydroxide in water [2].

Benzyltrimethylammonium hydroxide, Pyrrole

MCA Guide, 1972, 299

To catalyse the cyanoethylation of pyrrole, 3 drops of the basic catalyst solution were added to the reaction mixture of pyrrole (30%) in the nitrile. An exotherm developed and base-catalysed polymerisation of the nitrile accelerated to explosion.

See Bases, above

See also Tetrahydrocarbazole, etc., below

See other POLYMERISATION INCIDENTS

Formaldehyde

Personal experience

The reaction between acrylonitrile and formaldehyde (as paraformaldehyde or trioxane), under strong acid catalysis (usually sulphuric) and most often in presence of catalytic quantities of acetic anyhydride, to produce triacrylohexahydrotriazine, is inclined to violent exotherm after an induction period. The runaway can be uncontrollable on sub-molar scale. It may be due to acrylate polymerisation or to increasing reactivity of the formaldehyde equivalent due to progressive de-oligomerisation. Procedures claimed to prevent the risk have been described in the literature but do not seem reliable.

Halogens MRH 2.84/tr. Bromine

1. *MCA Case History No. 1214*
2. Towell, G., 1989, Personal communication

Bromine was being added in portions to acrylonitrile with ice cooling, with intermediate warming to 20°C between portions. After half the bromine was added, the temperature increased to 70°C; then the flask exploded. This was attributed either to an accumulation of unreacted bromine (which would be obvious) or to violent polymerisation [1]. The latter seems more likely, catalysed by hydrogen bromide formed by substitutive bromination. Chlorine produces similar phenomena, even if the flask stays intact. The runaway is preceded by loss of yellow colouration and accompanied by formation of 3-chloroacrylonitrile and derivatives. It can be suppressed by presence of bases [2].

See Acids, above

Initiators

1. Zhulin, V. M. *et al., Dokl. Akad. Nauk SSSR*, 1966, **170**, 1360—1363
2. Biesenberger, J. A. *et al., Polymer Eng. Sci.*, 1976, **16**, 101—116

At pressures above 6000 bar, free radical polymerisation sometimes proceeded explosively [1]. The parameters were determined in a batch reactor for thermal runaway polymerisation of acrylonitrile initiated by azoisobutyronitrile, dibenzoyl peroxide or di-*tert*-butyl peroxide [2].

See VIOLENT POLYMERISATION

See other POLYMERISATION INCIDENTS

Other reactants

Yoshida, 1980, 11

MRH values calculated for 17 combinations, mainly with oxidants, are given

Silver nitrate

Anon., *ABCM Quart. Safety Summ.*, 1962, **33**, 24

Acrylonitrile containing undissolved solid silver nitrate is liable, on long standing, to polymerise explosively and ignite. This was attributed to the slow deposition of a thermally insulating layer of polymer on the solid nitrate, which gradually gets hotter and catalyses rapid polymerisation. Photocatalysed decomposition of the salt with formation of traces of nitric acid may have been involved in the initial stages.

See other POLYMERISATION INCIDENTS

Tetrahydrocarbazole, Benzyltrimethylammonium hydroxide

Anon., *BCISC Quart. Safety Summ.*, 1968, **39**, 36

Cyanoethylation of 1,2,3,4-tetrahydrocarbazole initiated by the quaternary base had been effected smoothly on twice a published scale of working. During a further fourfold increase in scale, the initiator was added at 0°C, and shortly after cooling had been stopped and heating begun, the mixture exploded. A smaller proportion of initiator and very slow warming to effect reaction are recommended (to avoid rapid polymerisation of the nitrile by the base).

See Benzyltrimethylammonium hydroxide, etc., and Bases, both above

See other CYANO COMPOUNDS

See related HALOALKENES

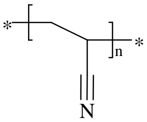
Trichloroacetyl chloride

Fakhraian, H. *et al., Org. Process R & D.*, 2003, **7**(6), 1040

Copper catalysed reaction of these two, under pressure, demonstrated potential for explosion when increased beyond low gram scale. Excess nitrile was in use as solvent, and the desired reaction is reported as very exothermic (~3 kJ/g of reagent mix).

1105. Poly(acrylonitrile)

[25014-41-9] **$(C_3H_3N)_n$**

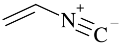


Methacrylate polymer, Nitric acid

See Nitric acid: Acrylonitrile—methacrylate copolymer

1106. Vinyl isocyanide (Isocyanoethene)

[14668-82-7] **C_3H_3N**



1. Matteson, D. S. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 3765
2. Bailey, R., *Chem. Abs.*, 1968, **69**, 113029

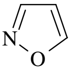
The molar heat of formation of this endothermic compound (+230—250 kJ, 4.5 kJ/g) is comparable with that of buten-3-yne (vinylacetylene). While no explosive decomposition of the isocyanide has been reported, the possibility should be borne in mind [1]. It is stable at —15°C, but isomerises to acrylonitrile and polymerises at ambient temperature [2].

See other ENDOTHERMIC COMPOUNDS

See related CYANO COMPOUNDS

†1107. Isoxazole

[288-14-2] **C_3H_3NO**



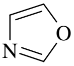
Sealed samples decompose exothermally above 136°C.

See entry ISOXAZOLES

See other N—O COMPOUNDS

†1108. Oxazole

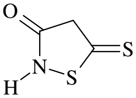
[288-42-6] **C_3H_3NO**



See other N—O COMPOUNDS

1109. 2-Thioxo-4-thiazolidinone (‘Rhodanine’)

[141-84-4] **$C_3H_3NOS_2$**



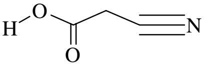
Merck, 1983, 1180

It may explode on rapid heating.

See other N—S COMPOUNDS

1110. Cyanoacetic acid

[372-09-8] **$C_3H_3NO_2$**



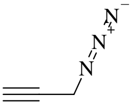
Furfuryl alcohol

See Furfuryl alcohol: Acids

See other CYANO COMPOUNDS, ORGANIC ACIDS

1111. 3-Azidopropyne (Propargyl azide)

[14989-89-0] **$C_3H_3N_3$**



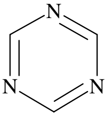
Almlof, J. *et al., J. Mol. Struct.*, 1987, **160**, 1

It is extremely explosive and must be handled with utmost care. Explosions during synthesis (100 mmol, 8.1 g) wrecked a ventilated hood. (The energy of decomposition of this endothermic acetylenic azide probably exceeds 250 kJ/mol, 3 kJ/g.)

See other ACETYLENIC COMPOUNDS, ENDOTHERMIC COMPOUNDS, ORGANIC AZIDES

1112. 1,3,5-Triazine

[290-87-9] **$C_3H_3N_3$**



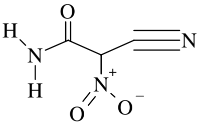
Nitric acid, Trifluoroacetic anhydride

See Nitric acid: Triazine, etc.

See other ORGANIC BASES

1113. 2-Carbamoyl-2-nitroacetonitrile (‘Fulminuric acid’)

[475-08-1] **$C_3H_3N_3O_3$**



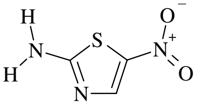
Sorbe, 1968, 74

It explodes on heating.

See other CYANO COMPOUNDS, C—NITRO COMPOUNDS

1114. 2-Amino-5-nitrothiazole

[121-66-4] **$C_3H_3N_3O_2S$**



CHETAH, 1990, 183

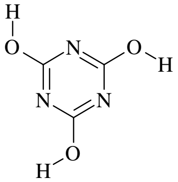
Can be exploded with a detonator, not by mechanical shock.

Preparative hazard

See Nitric acid: 2-Aminothiazole, Sulfuric acid

1115. 2,4,6-Trihydroxy-1,3,5-triazine (Cyanuric acid)

[108-80-5] **$C_3H_3N_3O_3$**

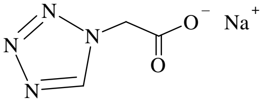


Chlorine

See Chlorine: Nitrogen compounds

1116. Sodium 1-tetrazolacetate

[51286-84-1] **$C_3H_3N_4NaO_2$**

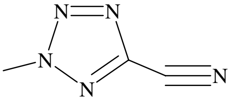


See Potassium 1-tetrazolacetate

See other TETRAZOLES

1117. 5-Cyano-2-methyltetrazole

[91511-39-6] **$C_3H_3N_5$**



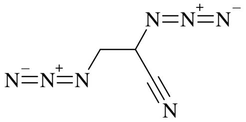
Aluminium hydride

See Aluminium hydride: Tetrazole derivatives

See other TETRAZOLES

1118. 2,3-Diazidopropiononitrile

[101944-90-5] **$C_3H_3N_7$**



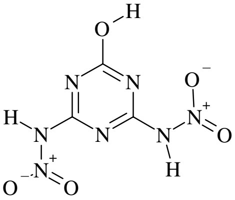
Owston, P. G. *et al., J. Chem. Res.; Synop.*, 1985, (11), 352—353

It is unstable and potentially explosive: routine use of a fume cupboard and safety screens is recommended.

See other CYANO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1119. 2-Hydroxy-4,6-bis(nitroamino)-1,3,5-triazine

[19899-80-0] **$C_3H_3N_7O_5$**



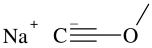
Atkinson. J. R., *J. Amer. Chem. Soc.*, 1951, **73**, 4443—4444

The explosive nitration product of ‘melamine’ was identified as the title compound of low oxygen balance, which is easily detonated on impact.

See other N—NITRO COMPOUNDS

1120. Sodium methoxyacetylide

[ ] **C_3H_3NaO**



Houben-Weyl, 1970, Vol. 13.1, 649

It may ignite in air.

Brine

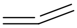
Jones, E. R. H. *et al., Org. Synth.*, 1963, Coll. Vol. 4, 406

During addition of saturated brine at —20°C to the sodium derivative at —70°C, minor explosions occur. These may have been caused by particles of sodium igniting the liberated methoxyacetylene.

See other METAL ACETYLIDES

†1121. Propadiene (Allene)

[463-49-0] **C_3H_4**



HCS 1980, 779 (cylinder)

1. Bondor, A. M. *et al., Khim. Prom.*, 1965, **41**, 923
2. Forshey, D. R., *Fire Technol.*, 1969, **5**, 100—111

The diene is endothermic (ΔH_f° (g) +192.1 kJ/mol, 4.80 kJ/g) and the pure gas can decompose explosively under a pressure of 2 bar [1], but this is also quoted as the upper limiting pressure for flame propagation during sustained (monopropellant) burning at 25°C [2].

See Propyne (below)

Oxides of nitrogen

See Nitrogen oxide: Dienes, Oxygen

See other DIENES, ENDOTHERMIC COMPOUNDS

†1122. Propyne

[74-99-7] **C_3H_4**

HCS 1980, 633 (cylinder)

1. *MCA Case History No. 632*
2. Fitzgerald, F., *Nature*, 1960, **186**, 386—387
3. Hurden, D., *J. Inst. Fuel.*, 1963, **36**, 50—54
4. Stull, 1977, 16

The liquid material in cylinders (which contains around 30% of propadiene) is not shock-sensitive, but a wall temperature of 95°C (even very localised) accompanied by pressures of about 3.5 bar, will cause a detonation to propagate from the hot spot [1]. Induced decomposition of the endothermic hydrocarbon leads to flame propagation in absence of air above minimum pressures of 3.4 and 2.1 bar at 20 and 120°C, respectively [2]. Application as a monopropellant and possible hazards therefrom (including formation of explosive copper propynide) have been discussed [3]. Although the pure material is highly endothermic (ΔH_f° (g) +185.4 kJ/mol, 4.64 kJ/g), the commercial mixture with propadiene and propane (MAPP gas) is comparable with ethylene for handling requirements and potential hazard [4].

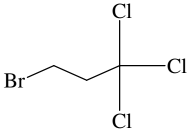
Silver nitrate

Grignard, 1935, Vol. 3, 175

Interaction in ammoniacal solution gives the silver derivative which ignites around 150°C.

See other ALKYNES, ENDOTHERMIC COMPOUNDS

1123. 3-Bromo-1,1,1-trichloropropane
[13749-37-6] **$C_3H_4BrCl_3$**

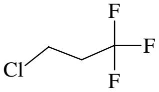


Preparative hazard

See Ethylene: Bromotrichloromethane

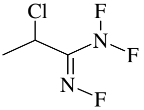
See other HALOALKANES

†1124. 1-Chloro-3,3,3-trifluoropropane
[460-35-5] **$C_3H_4ClF_3$**



See other HALOALKANES

1125. 2-Chloro-*N,N,N′*-trifluoropropionamidine
[25238-02-2] **$C_3H_4ClF_3N_2$**

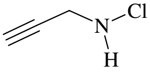


Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3096—3097

A shock-sensitive explosive.

See other *N,N,N′*-TRIFLUOROAMIDINES

1126. *N*-Chloro-3-aminopropyne (*N*-Chloropropargylamine)
[103698-31-3] **C_3H_4ClN**

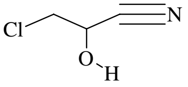


It explodes at ambient temperature.

See other ACETYLENIC COMPOUNDS, *N*-HALOGEN COMPOUNDS, *N*-HALOGEN COMPOUNDS (reference 4)

1127. 2-Chloro-1-cyanoethanol (3-Chlorolactonitrile)

[33965-80-9] **C_3H_4ClNO**



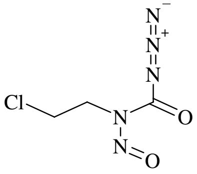
Scotti, F. *et al., J. Org. Chem.*, 1964, **29**, 1800

Distillation (at 110°C/4 mbar) is hazardous, since slight overheating may cause explosive decomposition to 2-chloroacetaldehyde and hydrogen cyanide.

See other CYANO COMPOUNDS

1128. *N*-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide

[60784-40-9] **$C_3H_4ClN_5O_2$**



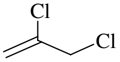
Eisenbrand, G., Ger. Offen. 2 659 862, 1978

It should not be isoated from solution, as it is potentially explosive.

See other ACYL AZIDES, NITROSO COMPOUNDS

†1129. 2,3-Dichloropropene

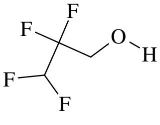
[78-88-6] **$C_3H_4Cl_2$**



See other HALOALKENES

1130. 2,2,3,3-Tetrafluoropropanol

[76-37-9] **$C_3H_4F_4O$**



Potassium hydroxide, or Sodium

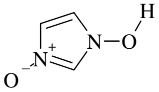
Bagnall, R. D., private comm., 1972

Attempted formation of sodium tetrafluoropropoxide by adding the alcohol to sodium (40 g) caused ignition and a fierce fire which melted the flask. This was attributed to alkoxide-induced elimination of hydrogen fluoride, and subsequent exothermic

polymerisation. In an alternative preparation of the potassium alkoxide by adding the alcohol to solid potassium hydroxide, a vigorous exotherm occurred. This was not seen when the base was added slowly to the alcohol.
See other POLYMERISATION INCIDENTS

1131. 1-Hydroxyimidazole *N*-oxide

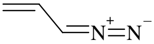
[35321-46-1] **$C_3H_4N_2O_2$**



Flynn, A. P., *Chem. Brit.*, 1984, **20**, 30
On DSC examination it exhibits a large decomposition exotherm at 200—250°C, and is a sensitive detonating and deflagrating explosive.
See 1-Methoxyimidazole *N*-oxide
See other N—O COMPOUNDS, *N*-OXIDES

1132a. 3-Diazopropene (Vinyldiazomethane)

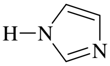
[2032-04-4] **$C_3H_4N_2$**



Salomon, R. G. *et al., J. Org. Chem.*, 1975, **40**, 758
Potentially explosive, it should be stored in solution at 0°C and shielded from light.
See other DIAZO COMPOUNDS

1132b. Imidazole

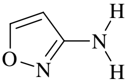
[288-32-4] **$C_3H_4N_2$**



Modestly endothermic: ΔH_f° (s) 50 kJ/mole, 0.8 kJ/g. Not a known source of hazard.
See other ENDOTHERMIC COMPOUNDS

1133. 3-Aminoisoxazole

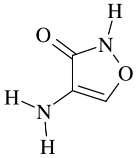
[1750-42-1] **$C_3H_4N_2O$**



Sealed samples decompose exothermally above 115°C.
See entry ISOXAZOLES
See other N—O COMPOUNDS

1134. 4-Amino-3-isoxazolidinone

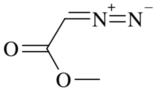
[68-39-3] **$C_3H_4N_2O_2$**



Sealed samples decompose exothermally above 78°C.
See entry ISOXAZOLES
See other N—O COMPOUNDS

1135. Methyl diazoacetate

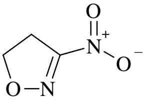
[6832-16-2] **$C_3H_4N_2O_2$**



Searle, N. E., *Org. Synth.*, 1963, Coll. Vol. 4, 426
This ester must be handled with particular caution as it explodes with extreme violence on heating.
See other DIAZO COMPOUNDS

1136. 3-Nitro-2-isoxazoline

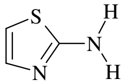
[1121-14-8] **$C_3H_4N_2O_3$**



CHETAH, 1990, 188
Shock sensitive
See other C—NITRO COMPOUNDS, N—O COMPOUNDS

1137. 2-Aminothiazole

[96-50-4] **$C_3H_4N_2S$**

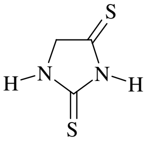


MCA Case History No. 1587
Drying 2-aminothiazole in an oven without forced air circulation caused development of hot spots and eventual ignition. It has a low auto-ignition temperature and will ignite after 3.5 h at 100°C.

Nitric acid
See Nitric acid: 2-Aminothiazole

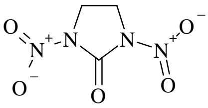
Nitric acid, Sulfuric acid
See Nitric acid: 2-Aminothiazole, Sulfuric acid

1138. Imidazoline-2,4-dithione ('Dithiohydantoin')
[5789-17-3] **$C_3H_4N_2S_2$**



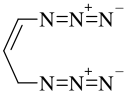
Pouwels, H., *Chem. Eng. News*, 1975, **53**(49), 5
A 70 g sample, sealed into a brown glass ampoule, exploded after storage at ambient temperature for 17 years. This was attributed to slow decomposition and gas generation (perhaps initiated by traces of alkali in the ampoule glass).
See Pyrimidine-2,4,5,6-(1*H*,3*H*)-tetraone
See other GLASS INCIDENTS

1139. 1,3-Dinitro-2-imidazolidinone
[2536-18-7] **$C_3H_4N_4O_5$**



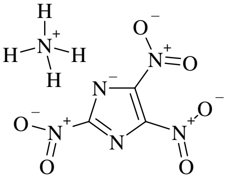
Violent decomposition occurred at 238°C.
See entry DIFFERENTIAL THERMAL ANALYSIS(DTA) (reference 1)
See other N—NITRO COMPOUNDS

1140. 1,3-Diazidopropene
[22750-69-2] **$C_3H_4N_6$**



Forster, M. O. *et al., J. Chem. Soc.*, 1912, **101**, 489
A sample exploded while being weighed.
See other ORGANIC AZIDES

1141. Ammonium 2,4,5-trinitroimidazolide
[63839-60-1] $C_3H_4N_6O_6$

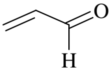


Coburn, M. D. US Pat. 4 028 154, 1977

The ammonium salt is an explosive comparable to RDX but of higher thermal stability.

See related POLYNITROARYL COMPOUNDS

†1142. Acrylaldehyde (Propenal)
[107-02-8] C_3H_4O



(*MCA SD-85*, 1961); *NSC 436*, 1978; *NFPA H49*, 1976; *HCS 1980*, 113; *RSC Lab. Hazards Data Sheet No. 70*, 1988

Energy of decomposition (in range 70—380°C) measured as 0.864 kJ/g by DSC, and T_{ait24} was determined as 117°C by adiabatic Dewar tests, with an apparent energy of activation of 214 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Acids, or Bases

1. *MCA SD-85*, 1961
2. Hearsey, C. J., private comm., 1973
3. Personal experience (PGU)
4. Catalogue note, Hopkin & Williams, 1973
5. Bond, J., *Loss Prev. Bull.*, 1985, (065), 26

Acrylaldehyde (acrolein) is very reactive and will polymerise rapidly, accelerating to violence, in contact with strong acid or basic catalysts. Normally an induction period, shortened by increase in contamination, water content or initial temperature, precedes the onset of polymerisation. Uncatalysed polymerisation sets in at 200°C in the pure material [1]. Exposure to weakly acidic conditions (nitrous fumes, sulfur dioxide, carbon dioxide), some hydrolysable salts, or thiourea will also cause exothermic and violent polymerisation. A 2 year old sample stored in a refrigerator close to a bottle of dimethylamine exploded violently, presumably after absorbing enough volatile amine (which penetrates plastics closures) to initiate polymerisation [2]. Measurement of acrolein in a plastic measuring cylinder previously used for triethylamine (and allowed to evaporate dry) gave rise to violent polymerisation and a lacquered fume cupboard within less than a minute [3]. The stabilising effect of the added hydroquinone may cease after a comparatively short storage time. Such unstabilised material could polymerise explosively [4]. Violent polymerisation in a 250 kl storage tank led to an explosion and widespread damage [5].

See other ALDEHYDES, CATALYTIC IMPURITY INCIDENTS, INDUCTION PERIOD INCIDENTS, PEROXIDISABLE COMPOUNDS, POLYMERISATION INCIDENTS

Trienes

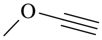
Anon., 1989, Personal communication

Calorimetric investigation of a Diels Alder reaction between propenal and a triene, which had caused problems on scale-up, showed, after the exotherm due to the Diels Alder reaction, and from a temperature a litle above 200°C, a second, more exothermic, reaction with a very fast pressure rise which burst the ARC can employed. This is presumably aromatisation of the alkenylcyclohexenealdehyde first formed, with probable liberation of hydrogen and carbon monoxide.

See ACCELERATING RATE CALORIMETRY

†1143. Methoxyacetylene (Ethynyl methyl ether)

[6443-91-0] **C_3H_4O**

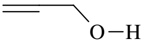


See Sodium methoxyacetylide: Brine

See other ACETYLENIC COMPOUNDS

1144. 3-Propynol (Propargyl alcohol)

[107-19-7] **C_3H_4O**



Alkalies

Anon., *Angew. Chem. (Nachr.)*, 1954, **2**, 209

If propynol and similar acetylenic compounds are dried with alkali before distillation, the residue may explode (probably owing to acetylenic salt formation). Sodium sulfate is recommended as a suitable desiccant.

Mercury(II) sulfate, Sulfuric acid, Water

1. Reppe, W. *et al., Ann.*, 1955, **596**, 38
2. Nettleton, J., private comm., 1972

Following the published procedure [1], hydroxyacetone was being prepared on half the scale by treating propargyl alcohol as a 30% aqueous solution with mercury sulfate and sulfuric acid (6 g and 0.6 g/mol of alcohol, respectively). On stirring and warming the mixture to 70°C a violent exothermic eruption occurred. Quartering the scale of operations to 1 g mol and reducing the amount of acid to 0.37 g/mol gave a controllable reaction at 70°C. Adding the alcohol to the other reactants at 70°C is an alternative possibility to avoid the suspected protonation and polymerisation of the propargyl alcohol.

See other POLYMERISATION INCIDENTS

Phosphorus pentaoxide

491M, 1975, 321

Addition of the (acidic) oxide to the alcohol caused ignition.

Sulfuric acid

1. Sauer, J. C., *Org. Synth.*, 1963, Coll. Vol. 4, 813
2. Crouse, D. M., *Chem. Eng. News*, 1979, **57**(41), 4
3. Hart, E. V., *Chem. Eng. News*, 1980, **58**(2), 4

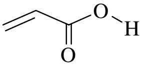
During addition of 56% aqueous acid to the aqueous 33% alcohol, using a published procedure for conversion to propiolaldehyde [1], a violent explosion was attributed to lack of adequate cooling [2]. This attribution is disputed, and contamination, possibly with a heavy metal ion, is postulated [3]. The published procedure is rated not hazardous.

See Mercury(II) sulfate, etc., above

See other ACETYLENIC COMPOUNDS

1145. Acrylic acid (Propenoic acid)

[79-10-7] **$C_3H_4O_2$**



FPA H95, 1980; *HCS 1980*, 115; *RSC Lab. Hazard Data Sheet No. 68*, 1988

1. *Haz Chem. Data*, 1975, 34
2. Anon., *RoSPA OS&H Bull.*, 1976, (10), 3
3. Anaorian, M. *et al., Eur. Polym. J.*, 1981, **17**, 823—838
4. Bond, J., *Loss Prev. Bull.*, 1985, (065), 26
5. Kurland, J. J. *et al., Plant/Oper. Progr.*, 1987, **6**, 203—207
6. Yassin, A. A. *et al., Chem. & Ind.*, 1985, 275
7. Levy, L. B., *Plant/Oper. Progr.*, 1987, **6**, 188—189; *ibid.*, 1989, **8**(2), 105
8. Wamper, F. M., *Plant/Oper. Progr.*, 1988, **7**, 183—189

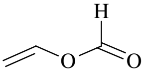
Acrylic acid is normally supplied as the inhibited monomer, but because of its relatively high freezing point (14°C) it often partly solidifies, and the solid phase (and the vapour) will then be free of inhibitor which remains in the liquid phase. Even the uninhibited acid may be stored safely below the m.p., but such material will polymerise exothermically at ambient temperature, and may accelerate to a violent or explosive state if confined. Narrow vents may become blocked by polymerisation of uninhibited vapour [1]. A 17 m^3 tank trailer of glacial acrylic acid was being warmed by internal coils containing water from an unmonitored steam and water mixer to prevent the acid freezing in sub-zero temperatures. The extremely violent explosion which occurred later probably involved explosive polymerisation accelerated by both the latent heat liberated when the acid froze, and the uncontrolled deliberate heating [2]. The detailed mechanism of auto-accelerating polymerisation of the acid in hexane—methanol solution, which becomes explosive, has been studied [3]. Contamination of a 220 kl cargo of acrylic acid from an adjacent storage tank in a marine tanker led to an escalating polymerisation which could not be controlled, and

the cargo could not be off-loaded. Eventually the tank had to be cut out of the ship [4]. It appears that the contaminant leaking into the acrylic acid was ethylidenenorbornene, which reacted with the traces of oxygen necessary to activate the inhibitor in the acrylic acid, leading to onset of polymerisation [5]. Hexamethylenetetramine is an effective stabiliser for acrylic acid in both liquid and vapour phases, preventing polymerisation at concentrations of 50—100 ppm [6]. Dimerisation of acrylic acid is temperature and solvent dependent and cannot be controlled by inhibitors, but vinyl polymerisation can be inhibited by conventional radical-trapping compounds, such as hydroquinone or phenothiazine, both of which need access of some oxygen for activation [7]. The dimerisation process of moist acrylic acid has been further investigated, and an empirical equation permits prediction of the extent of dimerisation in storage at different temperatures [8].
See other POLYMERISATION INCIDENTS

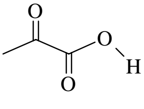
Initiator, Water
Anon., *Sichere Chemiearb.*, 1978, **30**, 3
During the experimental large scale continuous polymerisation of acrylic acid in aqueous solution in presence of an initiator and a moderator, failure of one of the feed pumps led to an unusually high concentration of monomer in solution. This led to runaway polymerisation which burst a glass vent line and the escaping contents ignited and led to an explosion and fire.
See other GLASS INCIDENTS, POLYMERISATION INCIDENTS

Other reactants
Yoshida, 1980, 8
MRH values calculated for 13 combinations with oxidants are given.
See VIOLENT POLYMERISATION
See other ORGANIC ACIDS

†1146. Vinyl formate (Ethenyl methanoate)
[692-45-5] **$C_3H_4O_2$**



1147a. Pyruvic acid (2-Oxopropanoic acid)
[127-17-3] **$C_3H_4O_3$**



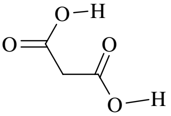
1. Anon., *Sichere Chemiearb.*, 1977, **29**, 87
2. Wolff, L., *Ann.*, 1901, **317**, 2

A bottle of analytical grade material exploded in laboratory storage at 25°C (undoubtedly from internal pressure of carbon dioxide). Pure material, protected from light and air, is only stable on a long term basis if kept refrigerated. Otherwise slow decomposition and decarboxylation occurs [1], possibly accelerated by enzymic catalysis from ingress of airborne yeasts. At ambient temperature, the acid dimerises and dehydrates to 2-oxo-4-carboxyvalerolactone [2].

See other GAS EVOLUTION INCIDENTS, ORGANIC ACIDS

1147b. Malonic acid (Propanedioic acid)

[141-82-2] **$C_3H_4O_4$**



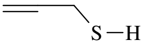
Although undoubtedly capable of generating carbon dioxide by thermal decomposition, the editor has heard of no pressurisation problems arising from this.

Potassium bromate, Ceric ammonium nitrate, Water

See Potassium bromate: Ceric ammonium nitrate, Malonic acid, Water

1148a. 3-Propynethiol

[27846-30-6] **C_3H_4S**



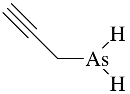
1. Sato, K. *et al., Chem. Abs.*, 1956, **53**, 5112b
2. Brandsma, 1971, 179

When distilled at ambient pressure, it polymerised explosively. It distils smoothly under reduced pressure at 33—35°C/127 mbar [1]. The polymer produced on exposure to air may explode on heating. Presence of a stabiliser is essential during handling or storage under nitrogen at —20°C [2].

See other ACETYLENIC COMPOUNDS, POLYMERISATION INCIDENTS

†1148b. 2-Propynylarsine (Propargylarsine)

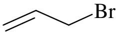
[254995-79-4] **C_3H_5As**



Guillemin, J-C. *et al., Organometallics*, 1999, **18**(25), 5259

See other ACETYLENIC COMPOUNDS, ALKYLMETAL HYDRIDES

†1149a. 3-Bromo-1-propene (Allyl bromide) (Prop-2-enyl bromide)
[106-95-6] **C_3H_5Br**



HCS 1980, 124

See other ALLYL COMPOUNDS, HALOALKENES

Ozone

See Ozone: Allyl bromide

1149b. Sodio(bromonitropropane)
[ ] **$C_3H_5BrNNaO_2$**

$C_3H_5BrNNaO_2$

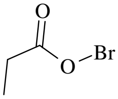
Ohio State University; www.chemistry.ohio-state.edu/safety

The sodium salt of a bromonitropropane (no isomer specified, but 1,1 most probable) was prepared on 10 g scale, dried and left in a vial. During the night, the vial exploded, damaging adjacent apparatus. Not only are nitroalkane salts unstable, but so are metal derivatives of halocarbons.

NITROALKANES: Alkali metals, or Inorganic bases

NITROALKENES

1150. Propionyl hypobromite
[82198-80-9] **$C_3H_5BrO_2$**

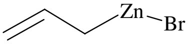


Skell, P. S. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 4000

As an isolated solid it is unpredictably explosive.

See other ACYL HYPOHALITES

1151. Allylzinc bromide (Bromo-2-propenylzinc)
[18925-10-5] **C_3H_5BrZn**

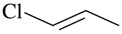


Formamide, Ketones

See Formamide: Organozinc compounds

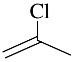
See also GRIGNARD REAGENTS

†1152. 1-Chloro-1-propene
[590-21-6] **C_3H_5Cl**



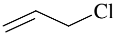
See other HALOALKENES

†1153. 2-Chloropropene
[557-98-2] **C_3H_5Cl**



See other HALOALKENES

†1154. 3-Chloropropene (Allyl chloride)
[107-05-1] **C_3H_5Cl**



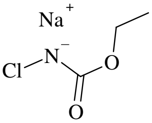
MCA SD-99, 1973); *HCS 1980*, 125; *RSC Lab. Hazards Data Sheet No. 28*, 1984

Piccinini, N. *et al., Plant/Operations Progr.*, 1982, **1**, 69—74
An operability analysis to identify potential risks in an allyl chloride manufacturing plant has been published.

Aromatic hydrocarbons, Ethylaluminium chlorides
491M, 1975, 22
Friedel-Crafts alkylation of benzene or toluene by allyl chloride in presence of ethylaluminium chlorides is vigorous even at —70°C, and explosions have occurred.
See Lewis acids, etc., next below

Lewis acids, Metals
MCA SD-99, 1973
Contact with aluminium chloride, boron trifluoride, sulfuric acid etc., may cause violently exothermic polymerisation. Organometallic products of contact of the chloride with aluminium, magnesium, zinc (or galvanised metal) may produce similar results.
See other ALLYL COMPOUNDS, HALOALKENES

1155. Ethyl *N*-chloro-*N*-sodiocarbamate
[17510-52-0] **$C_3H_5ClNNaO_2$**



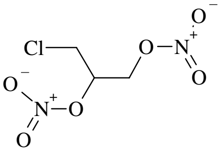
1. Herranz, E. *et al., J. Amer. Chem. Soc.*, 1978, **100**, 3598, footnote 8
2. Scully, F. E., *Tetrahedron Lett.*, 1990, **31**(37), 5261

It may decompose (non-explosively) exothermally with gas evolution, and the scale of preparation should be limited to 0.2 g mol [1]. Samples drying in desiccators several times shattered them. Use in solution is recommended [2].

See other N-HALOGEN COMPOUNDS

1156. 1-Chloro-2,3-propylene dinitrate

[2612-33-1] **$C_3H_5ClN_2O_6$**



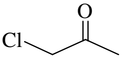
Sorbe, 1968, 54

An explosive syrup.

See related ALKYL NITRATES

1157. Chloroacetone (Chloro-2-propanone)

[78-95-5] **C_3H_5ClO**



HCS 1980, 291

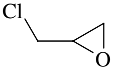
1. Allen, C. F. H. *et al., Ind. Eng. Chem. (News Ed.)*, 1931, **9**, 184
2. Ewe, G. E., *Ind. Eng. Chem. (News Ed.)*, 1931, **9**, 229

Two separate incidents involved explosive polymerisation of chloroacetone stored in glass bottles under ambient conditions for extended periods were reported [1,2].

See Bromoacetone oxime

†1158. 1-Chloro-2,3-epoxypropane (Chloromethyloxirane) (Epichlorohydrin)

[106-89-8] **C_3H_5ClO**



HCS 1980, 454

Energy of decomposition (in range 375—500°C) measured as 0.5 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Aniline

Hearfield, F., *Chem. Abs.*, 1980, **92**, 115649

In a review of thermal instability in chemical reactors, the explosive interaction of ‘epichlorohydrin’ with aniline is detailed.

Catalyst, Heterocyclic nitrogen compounds

Anon., *Sichere Chemiearb.*, 1985, **37**, 81

The epoxide and the nitrogen compound were mixed and stirred in a 250 l reactor fitted for reflux and protected by a rupture disk. After addition of the catalyst, subsequent heating to the required temperature seems to have been effected by direct application of steam to the jacket, rather than the usual hot water. The too-rapid heating led to a violently exothermic reaction which ruptured the disk and stretched the lid clamping bolts.

Contaminants

1. TV News item, ITN, 5th January, 1984
2. Sittig, 1981, 293

A road tanker was loaded with 1-chloro-2,3-epoxypropane and then driven 250 miles overnight to the delivery point. On arrival, the contents were found to have self heated (undoubtedly from polymerisation initiated by some unknown contaminant) to the boiling point (115°C at ambient pressure) and soon afterwards the relief valve lifted and discharged large volumes of vapour. Cooling with water sprays eventually restored thermal control over the remaining tanker contents [1]. The material is incompatible with strong acids, caustic alkalies, zinc, aluminium, aluminium chloride or iron(III) chloride, all of which catalyse exothermic polymerisation [2].

See other CATALYTIC IMPURITY INCIDENTS, POLYMERISATION INCIDENTS

Isopropylamine

Barton, N. *et al., Chem. & Ind.*, 1971, 994

With slow mixing and adequate cooling, smooth condensation to 1-chloro-3-isopropylamino-2-propanol occurs. With rapid mixing and poor cooling, a variable induction period with slow warming precedes a rapid, violent exotherm (to 350°C in 6 s). Other primary and secondary amines behave similarly. Moderating effects of water and the nature of the products are discussed.

See N-Substituted aniline, below

See other AMINATION INCIDENTS, INDUCTION PERIOD INCIDENTS

Potassium *tert*-butoxide

See Potassium *tert*-butoxide: Acids, etc.

Sodium chlorite

Anon. *Chemical Engineer*, 1996, (620), 4; *ibid*, 1996, (621),7

A tanker of aqueous ‘sodium chlorite’ was part charged to a tank of epichlorohydrin before it was reported it was mis-labelled. There was a very violent subsequent explosion, which blew down the wall of an adjacent factory. (The editor suspects it was, in fact, sodium hypochlorite, commonly known simply as hypochlorite, which sounds like epichlorohydrin. Sodium hypochlorite would be expected to be the more reactive of the two, generating an alkyl hypochlorite.)

See HYPOHALITES

N-Substituted aniline (unspecified)

Schierwater, F.-W., *Major Loss Prevention*, 1971, 47

Interaction is exothermic and the mixture was normally maintained at 60°C by stirring and cooling. Malfunction caused a temperature increase to 70°C and cooling capacity was insufficent to regain control. The temperature steadily increased to 120°C, when explosive decomposition occurred. This was attributed to thermal instability of the reaction system and inadequate pressure relief arrangements.

See Isopropylamine, above

Sulfuric acid

Leleu, *Cahiers*, 1974, (75), 276

Interaction is violent.

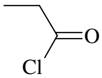
Trichloroethylene

See Trichloroethylene: Epoxides

See other 1,2-EPOXIDES

†1159. Propionyl chloride (Propanoyl chloride)

[79-03-8] **C_3H_5ClO**



HCS 1980, 794

Diisopropyl ether

Koenst, W. M. B., *J. Haz. Mat.*, 1981, **4**, 291—298

A facile exothermic reaction, catalysed by traces of zinc chloride and iron(III) chloride (4 and 40 ppm, respectively) to produce isopropyl propionate and 2-chloropropane (b.p., 35°C) led to pressure build up and bursting of a closed galvanised drum after 24 h. Similar reactions are thermodynamically possible with other acid chlorides and ethers (particularly if secondary or tertiary alkyl ethers), so such mixtures should only be prepared immediately prior to use.

See Sulfinyl chloride: Esters, Metals

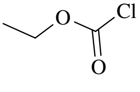
See other ACYL HALIDES, CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

Preparative hazard

See Phosphorus trichloride: Carboxylic acids

†1160. Ethyl chloroformate (Ethyl carbonochloridate)

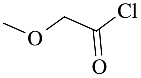
[541-41-3] **$C_3H_5ClO_2$**



HCS 1980, 476

See other ACYL HALIDES

1161. Methoxyacetyl chloride (2-Methoxyethanoyl chloride)
[38870-89-2] $C_3H_5ClO_2$

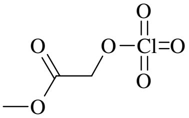


Anon., *Jahresber.*, 1979, 75

A sample of redistilled material in a screw capped bottle exploded 15 weeks after capping. This was attributed to development of internal pressure (probably of hydrogen chloride arising from hydrolysis, and perhaps also of chloromethane from scission). (The editor has also known methoxyacetic mixed anhydrides to decarbonylate, releasing carbon monoxide)

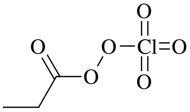
See other ACYL HALIDES, GAS EVOLUTION INCIDENTS

1162. Methoxycarbonylmethyl perchlorate
[95407-67-3] $C_3H_5ClO_6$



See entry ALKYL PERCHLORATES (reference 6)

1163. Peroxypropionyl perchlorate
[66955-44-0] $C_3H_5ClO_6$



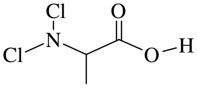
Yakarka, A. A. *et al., Chem. Abs.*, 1979, **91**, 210847

The oxidant exploded on detonation or friction.

See other NON-METAL PERCHLORATES, ORGANIC PEROXIDES

See related ACID ANHYDRIDES

1164. *N,N*-Dichloro-*β*-alanine (2-Dichloroaminopropanoic acid)
[58941-15-4] $C_3H_5Cl_2NO_2$

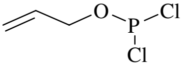


Vit, J. *et al., Synth. Commun.*, 1976, **6**(1), 1—4

It is thermally unstable above 95°C.

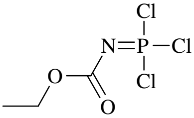
See other N-HALOGEN COMPOUNDS

1165. Allyl phosphorodichloridite
[1498-47-1] **$C_3H_5Cl_2OP$**



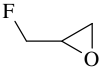
Kamler, M. *et al., Can. J. Chem.*, 1985, **63**, 825—826
The title compound is formed by reaction of allyl alcohol with phosphorus trichloride and is reported to polymerise explosively if the material, when being purified by distillation, is taken down to less than half its bulk.
See other ALLYL COMPOUNDS, PHOSPHORUS ESTERS

1166. *N*-Carboethoxyiminophosphoryl chloride
[3356-63-6] **$C_3H_5Cl_3NO_2P$**



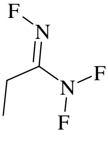
See N-Carbomethoxyiminophosphoryl chloride
See related NON-METAL HALIDES

†1167. 1-Fluoro-2,3-epoxypropane (Fluoromethyloxirane)
[503-09-3] **C_3H_5FO**



See other 1,2-EPOXIDES

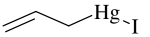
1168. *N,N,N′*-Trifluoropropionamidine
[21372-60-1] **$C_3H_5F_3N_2$**



Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3096—3097
A shock-sensitive explosive.
See other N,N,N′-TRIFLUOROAMIDINES

1169a. Allylmercury(II) iodide

[2845-00-3] **C_3H_5HgI**



Potassium cyanide

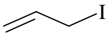
Whitmore, 1921, 122

Among the products of interaction, a minor one is an explosive liquid.

See other ALLYL COMPOUNDS, MERCURY COMPOUNDS

†1170. 3-Iodopropene (Allyl iodide)

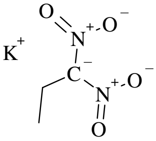
[556-56-9] **C_3H_5I**



See other ALLYL COMPOUNDS, HALOALKENES, IODINE COMPOUNDS

1171. Potassium 1,1-dinitropropanide

[30533-63-2] **$C_3H_5KN_2O_4$**



Bisgrove, D. E. *et al., Org. Synth.*, 1963, Coll. Vol. 4, 373

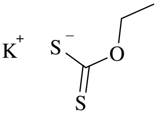
The potassium salt of 1,1-dinitropropane, isolated as a by-product during preparation of 3,4-dinitro-3-hexene, is a hazardous explosive.

See NITROALKANES: ALKALI METALS

See other POLYNITROALKYL COMPOUNDS

1172. Potassium *O*-ethyl dithiocarbonate ('Potassium ethyl xanthate')

[140-89-6] **$C_3H_5KOS_2$**

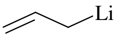


Diazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES

1173. Allyllithium

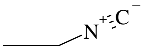
[3052-45-7] **C_3H_5Li**



Leleu, *Cahiers*, 1977, (88), 367
As usually prepared, it is a pyrophoric solid.
See other ALKYLMETALS, ALLYL COMPOUNDS

1174. Ethyl isocyanide (Isocyanoethane)

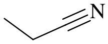
[624-79-3] **C_3H_5N**



Lemoult, M. P., *Compt. rend.*, 1906, **143**, 903
This showed a strong tendency to explode while being sealed into glass ampoules.
See Methyl isocyanide
See related CYANO COMPOUNDS

†1175. Propiononitrile (Propanonitrile)

[107-12-0] **C_3H_5N**

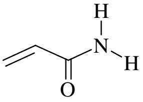


N-Bromosuccinimide
See N-Bromosuccinimide: Propiononitrile
See other CYANO COMPOUNDS

Preparative hazard
See Nitric acid: Aliphatic amines

1176. Acrylamide (Propenamide)

[79-06-1] **C_3H_5NO**

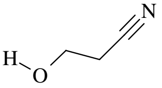


HCS 1980, 114

1. Bretherick, 1981, 165
2. Editor, 2004

It may polymerise with violence on melting at 86°C [1]. The concentrated aqueous solutions of commerce will crystallise in cool weather. The usual industrial technique for softening raw materials, applying a steam hose to the bottom of the container, to which crystals have fallen, will create domains of molten, unstabilised, monomer, initiating polymerisation of the whole, then rupturing containers through steam pressure. Rather, the liquid at the top should be warmed and circulated. Photoinitiation seems involved, black plastic containers give less problem than translucent ones. Best: do not store below 15°C [2].
See other POLYMERISATION INCIDENTS

1177. 2-Cyanoethanol (3-Hydroxypropanenitrile)
[109-78-4] **C_3H_5NO**



HCS 1980, 479

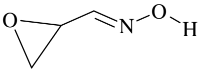
Acids, or Bases

HCS 1980, 479

Reacts violently with mineral acids, amines or inorganic bases, probably because of dehydration to acrylonitrile and subsequent catalysed polymerisation of the latter.

See other CYANO COMPOUNDS, POLYMERISATION INCIDENTS

1178. 2,3-Epoxypropionaldehyde oxime (Oxiranecarboxaldehyde oxime)
[67722-96-7] **$C_3H_5NO_2$**



Payne, G. B., *J. Amer. Chem. Soc.*, 1959, **81**, 4903

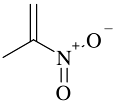
The residue from distillation at 48—49°C/1.3 mbar polymerised violently, and the distilled material polymerised explosively after 1—2 h at ambient temperature.

See 2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone

See other 1,2-EPOXIDES, OXIMES, POLYMERISATION INCIDENTS

See related ALDEHYDES

1179. 2-Nitropropene
[4749-28-4] **$C_3H_5NO_2$**

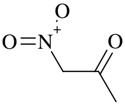


Miyashita, M. *et al., Org. Synth.*, 1981, **60**, 101—103

Vacuum distillation must be effected at below 80°C to avoid fume-offs, particularly if air be admitted to the warm residue. The lachrymatory material also polymerises in contact with alkalies.

See other NITROALKENES, POLYMERISATION INCIDENTS

1180. Nitroacetone (1-Nitro-2-propanone)
[10230-68-9] **$C_3H_5NO_3$**



1. Tegeler, J. J., *Chem. Eng. News*, 1987, **65**(1), 4
2. Author's comment, 1987

Nitroacetone (237 g) was generated in dichloromethane—ethyl acetate solution by treating its dicyclohexylamine *aci*-salt with sulfuric acid. Towards the end of concentration of the solution by rotary vacuum evaporation at 40—50°C, a small explosion occurred. Extreme caution and small scale handling of α-nitroketones are urged [1]. If exact neutralisation of the dicyclohexylamine salt had not been achieved, presence of excess sulfuric acid (or of some undecomposed *aci*-salt) may have reduced the stability of the nitroacetone [2].

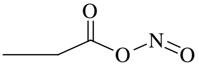
See Nitromethane: Acids, or Bases;

See also aci-NITRO SALTS

See related NITROALKANES

1181. Propionyl nitrite

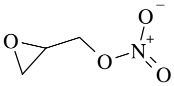
[28128-14-5] **$C_3H_5NO_3$**



See entry ACYL NITRITES

1182. 2,3-Epoxypropyl nitrate (Oxiranemethanol nitrate)

[6659-62-7] **$C_3H_5NO_4$**



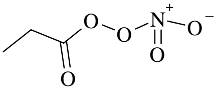
Urbanski, 1965, Vol. 2, 129

Shock-sensitive and explodes at 200°C.

See related ALKYL NITRATES, 1,2-EPOXIDES

1183. Peroxypropionyl nitrate

[5796-89-4] **$C_3H_5NO_5$**



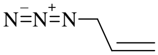
1. Stephens, E. R., *Anal. Chem.*, 1964, **36**, 928—929
2. Louw, R. *et al., J. Amer. Chem. Soc.*, 1975, **97**, 4396

Like the lower homologues, it is extremely explosive [1], and may only be handled in high dilution with air or nitrogen. Higher homologues are less explosive [2].

See related ACID ANHYDRIDES, ACYL NITRATES, PEROXYESTERS

1184. 3-Azidopropene (Allyl azide)

[821-13-6] **$C_3H_5N_3$**



1. Anon., *Saf. Digest*, (Univ. Saf. Assoc.), 1985, (13), 2—3
2. Forster, M. O., *J. Chem. Soc.*, 1908, **93**, 1174

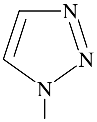
An explosion occurred in the final stages of evaporation of ether from allyl azide [1]. Peroxides in the ether may possibly have been involved, but the azide itself is of limited thermal stability, though apparently capable of distillation at 76°C/1 bar. The vapour is weakly explosive [2].

See other ALLYL COMPOUNDS, ORGANIC AZIDES

1185. 1-Methyl-1,2,3-triazole

[16681-65-5] **$C_3H_5N_3$**

Anon., private comm., 1980

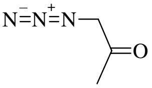


An explosion during the preparation of the triazole was attributed to local overheating or presence of impurities.

See other HIGH-NITROGEN COMPOUNDS, TRIAZOLES

1186. Azidoacetone (Azido-2-propanone)

[4504-27-2] **$C_3H_5N_3O$**



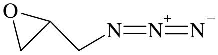
1. Spauschus, H. O. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 209
2. Forster, M. O. *et al., J. Chem. Soc.*, 1908, **93**, 72

A small sample exploded after storage in the dark for 6 months [1]. The freshly prepared material explodes when dropped on to a hotplate and burns brilliantly [2].

See other 2-AZIDOCARBONYL COMPOUNDS

1187. Glycidyl azide (Azidomethyloxirane)

[80044-09-3] [80044-10-6] polymer(—$CH_2CHOHCH_2(N_3)$—)$_n$ **$C_3H_5N_3O$**



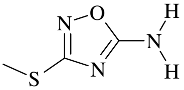
Nazare, A. N. *et al., J. Energ. Mater.*, 1992, **10**(1), 43

A review on the derived polymer as a propellant component, which use depends upon the energy of the azide. The monomer would be expected to have several kJ/g, including oxirane ring strain.

See 1,2-EPOXIDES, ORGANIC AZIDES

1188. 5-Amino-3-methylthio-1,2,4-oxadiazole

[55864-39-6] **$C_3H_5N_3OS$**



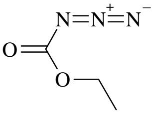
Wittenbrook, L. S., *J. Heterocycl. Chem.*, 1975, **12**, 38

It undergoes rapid and moderately violent decomposition at the m.p., 97—99°C.

See other N—O COMPOUNDS

1189. Ethyl azidoformate (Ethyl carbonazidate)

[817-87-8] **$C_3H_5N_3O_2$**



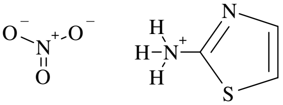
Forster, M. O. *et al., J. Chem. Soc.*, 1908, **93**, 91

It is liable to explode if boiled at ambient pressure (at 114°C). The methyl ester (b.p. 103°C) can behave similarly.

See other ACYL AZIDES

1190. 2-Ammoniothiazole nitrate

[57530-25-3] **$C_3H_5N_3O_3S$**



1. Rebsch, M., *Proc. Int. Symp. Prev. Occ. Risks Chem. Ind.*, 485—486, Heidelberg, ISSA., 1976
2. Soldarna Marlor, L., *Chem. Abs.*, 1977, **87**, 203834

During air-pressurised discharge of a hot 53% aqueous solution of the nitrate salt from a reaction vessel via a filter press, a violent explosion occurred. The nitrate salt begins to decompose below 100°C, and at the likely internal temperature of 142°C, decomposition would be expected to be very rapid, involving much gas/vapour generation according to the equation below.

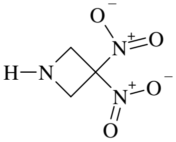
$$4C_3H_5N_3O_3S \not\Rightarrow 12C + 10H_2O + 6N_2 + 3S + SO_2$$

Air-pressurisation would have prevented the water from boiling and absorbing the exotherm to moderate the thermal explosion. Decomposition of the solution may have been accelerated by the presence of impurities, or by the solid salt splashed onto the heated vessel wall [1]. There is an independent account of the incident [2].

See other GAS EVOLUTION INCIDENTS

1191. 3,3-Dinitroazetidine

[129660-17-9] **$C_3H_5N_3O_4$**



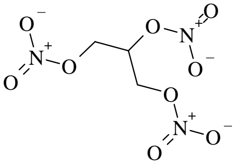
Hiskey, M. A. *et al., J. Energ. Mater.*, 1993, **11**(3), 157.

Dinitroazetidine salts were studied as explosives: nitrate, dinitroimidate, 2,4-dinitroimidazolate, 4,4′,5,5′-tetranitro-2,2′-biimidazolate, 5-nitro-1,2,4-triazolonate and 3,5-dinitrotriazolate.

See other C-NITRO COMPOUNDS, STRAINED-RING COMPOUNDS

1192a. Glyceryl trinitrate (1,2,3-Propanetriyl nitrate)

[55-63-0] **$C_3H_5N_3O_9$**



1. Urbanski, 1965, Vol. 2, 47, 53—54
2. Bond, J., *Loss Prev. Bull.*, 1983, (050), 18

The relatively high sensitivity of the pure liquid material to initiation by shock or heating (it explodes at 215—218°C, and decomposes energetically above 145°C) is enhanced by presence of impurities, especially nitric acid, arising from imperfect washing, hydrolysis or thermal aging (e.g. heating to 50°C). Intense UV radiation will explode a sample at 100°C. The sensitivity of the viscous liquid to shock is slightly reduced by freezing, but is greatly diminished by absorption onto porous solids, as in dynamite [1]. Many incidents, some dating back to 1870, are summarised, all involving violent explosions when cans or buckets of nitroglycerine were dropped. Some of these detonations initiated the detonation of bulk material nearby [2].

See other ALKYL NITRATES, IRRADIATION DECOMPOSITION INCIDENTS

†1192b. 2-Propynylphosphine (Propargylphosphine)

[114596-02-0] **C_3H_5P**

$HC{\equiv}CCH_2PH_2$

Guillemin, J-C. *et al., Organometallics*, 1999, **18**(25), 5259

See other ACETYLENIC COMPOUNDS, ALKYLMETAL HYDRIDES

†1193. Cyclopropane

[75-19-4] **C_3H_6**

HCS 1980, 351 (cylinder)

Stull, 1977, 16

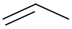
It is fairly endothermic and of low MW (ΔH_f° (g) +82.3 kJ/mol, 1.96kJ/g), and a minor constituent of MAPP gas.

See Propyne

See other ENDOTHERMIC COMPOUNDS, STRAINED-RING COMPOUNDS

†1194. Propene (Propylene)

[115-07-1] **C_3H_6**



(*MCA SD-59*, 1956); *FPA H75*, 1978; *HCS 1980*, 788 (cylinder)

1. Russell, F. R. *et al., Chem. Eng. News*, 1952, **30**, 1239
2. Stull, 1977, 16

Propene at 955 bar and 327°C was being subjected to further rapid compression. At 4.86 kbar explosive decomposition occurred, causing a pressure surge to 10 kbar or above. Decomposition to carbon, hydrogen and methane must have occurred to account for this pressure. Ethylene behaves similarly at much lower pressure, and cyclopentadiene, cyclohexadiene, acetylene and a few aromatic hydrocarbons have been decomposed explosively [1]. It is mildly endothermic (ΔH_f° (g) +20.4 kJ/mol, 0.49kJ/g) and a minor constituent of MAPP gas [2].

Air or Oxygen

Several sets of values for flammability limits in air are quoted; 1.4—7.1, 2.4—11.1, 2.7—36.0 vol%.

See also OXYGEN ENRICHMENT

Lithium nitrate, Sulfur dioxide

Pitkethly, R. C., private comm., 1973

A mixture under confinement in a glass pressure bottle at 20°C polymerised explosively, the polymerisation probably being initiated by access of light through the clear

glass container. Such alkene—sulfur dioxide co-polymerisations will not occur above a ceiling temperature, different for each alkene.
See other GLASS INCIDENTS, POLYMERISATION INCIDENTS

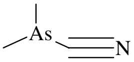
Other reactants
Yoshida, 1980, 321
MRH values calculated for 13 combinations with oxidants are given.

Oxides of nitrogen
See Nitrogen oxide: Dienes, Oxygen

Trifluoromethyl hypofluorite
See Trifluoromethyl hypofluorite: Hydrocarbons

Water
See LIQUEFIED GASES: Water
See other ALKENES

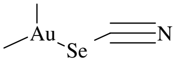
1195. Cyanodimethylarsine
[683-45-4] **C_3H_6AsN**



1. *491M*, 1975, 140
2. Cardillo. P. J. *Loss Prevention Proc. Ind.*, 2001, **14**, 75

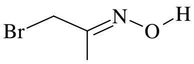
It ignites in air [1]. Following loss of an eye to an explosion when working with this compound, Bunsen forsook organic chemistry [2]
See related ALKYLNON-METAL HALIDES

1196. Dimethylgold selenocyanate
[42495-76-1] **C_3H_6AuNSe**



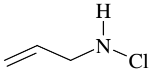
Stocco, F. *et al., Inorg. Chem.*, 1971, **10**, 2640
Very shock-sensitive and explodes readily when precipitated from aqueous solution. Crystals obtained by slow evaporation of a carbon tetrachloride extract were less sensitive.
See other GOLD COMPOUNDS
See related METAL CYANATES

1197. Bromoacetone oxime (1-Bromo-2-oximinopropane)
[62116-25-0] **C_3H_6BrNO**



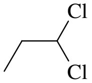
Forster, M. O *et al., J. Chem. Soc.*, 1908, **93**, 84
It decomposes explosively during distillation.
See Chloroacetaldehyde oxime, *and* Chloroacetone
See other OXIMES

1198. *N*-Chloroallylamine (*N*-Chloro-3-aminopropene)
[82865-33-6] **C_3H_6ClN**



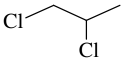
It explodes at ambient temperature.
See entry N-HALOGEN COMPOUNDS (reference 4)
See other ALLYL COMPOUNDS

†1199. 1,1-Dichloropropane
[78-99-9] **$C_3H_6Cl_2$**



See other HALOALKANES

†1200. 1,2-Dichloropropane
[78-87-5] **$C_3H_6Cl_2$**

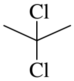


HCS 1980, 383

Aluminium
See Aluminium: Halocarbons (reference 18)

Aluminium, 1,2-Dichlorobenzene, 1,2-Dichloroethane
See Aluminium: Halocarbons (reference 5)
See other HALOALKANES

1201. 2,2-Dichloropropane
[594-20-7] **$C_3H_6Cl_2$**



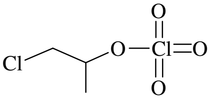
Dimethylzinc

See Dimethylzinc: 2,2-Dichloropropane

See other HALOALKANES

1202. 1-Chloro-2-propyl perchlorate

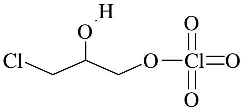
[58426-27-0] **$C_3H_6Cl_2O_4$**



See entry ALKYL PERCHLORATES (reference 6)

1203. 3-Chloro-2-hydroxypropyl perchlorate

[101672-07-5] **$C_3H_6Cl_2O_5$**



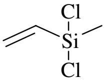
Hofmann, K. A. *et al., Ber.*, 1909, **42**, 4390

It explodes violently on shaking in a capillary.

See other ALKYL PERCHLORATES

†1204. Dichloromethylvinylsilane

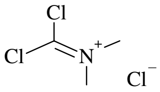
[124-70-9] **$C_3H_6Cl_2Si$**



See related ALKYLHALOSILANES

1205a. Dichloromethylenedimethylammonium chloride

[33842-02-3] **$C_3H_6Cl_3N$**



1. Bader, A. R., private comm., 1971
2. Senning, A., *Chem. Rev.*, 1965, **65**, 388

The compound does not explode on heating [1]; the earlier reference [2] is in error.

†1205b. 2-Propynylgermane (Propargylgermane)

[254995-80-1] **C_3H_6Ge**

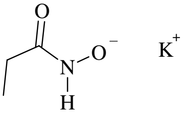
$$HC{\equiv}CCH_2GeH_3$$

Guillemin, J-C. *et al., Organometallics*, 1999, **18**(25), 5259

See other ACETYLENIC COMPOUNDS, ALKYLMETAL HYDRIDES

1206. Potassium *O*-propionohydroxamate

[71939-10-1] **$C_3H_6KNO_2$**



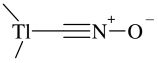
Anon., *Actual. Chim. (Fr.)*, 1983, **8**, 49—50

The solid explodes on attempted drying. DTA indicates that the rapid decomposition at 70—74°C to potassium hydroxide and ethyl isocyanate, accompanied by an exotherm of 1.37 kJ/g, is involved in the explosion.

See other N—O COMPOUNDS

1207. Dimethylthallium fulminate

[ ] **C_3H_6NOTl**



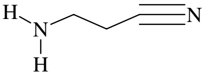
Beck, W. *et al., J. Organomet. Chem.*, 1965, **3**, 55

Highly explosive, unlike the diphenyl analogue.

See related METAL FULMINATES

1208. 3-Aminopropiononitrile

[151-18-8] **$C_3H_6N_2$**



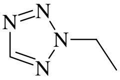
1. Shner, V. F., *Zhur. Prikl. Khim.*, 1966, **39**, 2386 (Engl. transl.)
2. *MCA Guide*, 1972, 309
3. Merck, 1976, 65

Vacuum distilled material kept dark for 6 months was found to have largely polymerised to a yellow solid, which exploded 15 days later [1]. A bottle of uninhibited distilled material exploded after shelf storage for several months [2]. It may be stored for several months out of contact with air under refrigeration. In contact with ambient air, it polymerises slowly, but rapidly in contact with acidic materials [3].

See other CYANO COMPOUNDS, POLYMERISATION INCIDENTS

1209. 2-Ethyltetrazole

[82944-28-3] **$C_3H_6N_4$**



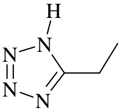
Aluminium hydride

See Aluminium hydride: Tetrazole derivatives

See other TETRAZOLES

1210. 5-Ethyltetrazole

[50764-78-8] **$C_3H_6N_4$**



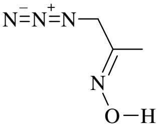
Aluminium hydride

See Aluminium hydride: Tetrazole derivatives

See other TETRAZOLES

1211. Azidoacetone oxime

[101672-04-2] **$C_3H_6N_4O$**



Forster, M. O. *et al., J. Chem. Soc.*, 1908, **93**, 83

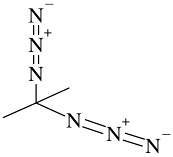
During distillation at 84°C/2.6 mbar, the large residue darkened and finally exploded violently.

See Bromoacetone oxime

See other 2-AZIDOCARBONYL COMPOUNDS

1212. 2,2-Diazidopropane

[85620-95-7] **$C_3H_6N_6$**



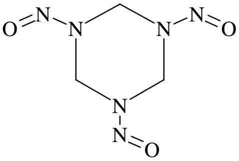
Al-Khalil, S. I. *et al., J. Chem. Soc., Perkin Trans. 1*, 1986, 555—565

The liquid azide, b.p. 28—30°C/0.6 mbar, exploded during attempted analytical combustion.

See other ORGANIC AZIDES

1213. 1,3,5-Trinitrosohexahydro-1,3,5-triazine

[13980-04-6] **$C_3H_6N_6O_3$**



Sulfuric acid

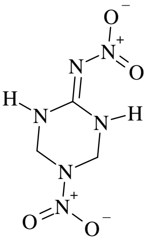
Urbanski, 1967, Vol. 3, 122

It decomposes explosively in contact with conc. sulfuric acid.

See other NITROSO COMPOUNDS

1214. 5-Nitro-2-(nitroimino)hexahydro-1,3,5-triazine (1,4,5,6-Tetrahydro-*N*,5-dinitrotriazin-2-amine)

[130400-13-4] **$C_3H_6N_6O_4$**



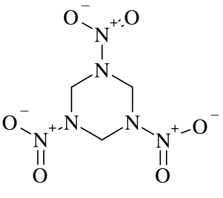
Dagley, I. J., *et al., J. Energ. Mater.*, 1995, **13**(1&2), 35

This nitroguanidine analogue is more sensitive than RDX by the drop-weight impact test.

See other N—NITRO COMPOUNDS

1215. 1,3,5-Trinitrohexahydro-1,3,5-triazine (Cyclotrimethylenetrinitramine)

[121-82-4] **$C_3H_6N_6O_6$**



Botcher, T. R. *et al., J. Amer. Chem. Soc.*, 1992, **114**(2), 8303

Some studies relating to the explosion mechanism of this military explosive (RDX or Cyclonite) and its higher homologue HMX.

Calcium hydroxide, Water

Iida, M. *et al., Chem. Abs.*, 1988, **109**, 112968

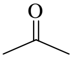
The self-heating and decomposition of the explosive and aqueous alkali was studied by DSC in a sealed capsule and in a larger scale furnace test. A rapid exothermic decomposition reaction can be initiated at 100°C or below, and may lead to spontaneous ignition and then deflagration or detonation.

See also NITROAROMATIC—ALKALI HAZARDS

See other *N*-NITRO COMPOUNDS

†1216. Acetone (2-Propanone)

[67-64-1] **C_3H_6O**



(*MCA SD-87*, 1962); *NSC 398*, 1982; *FPA H1*, 1972; *HCS 1980*, 102;
RSC Lab. Hazard Data Sheet No. 21, 1984

Bromoform

See Bromoform: Acetone, etc.

Carbon, Air

Boiston, D. A., *Brit. Chem. Eng.*, 1968, **13**, 85

(In the absence of other ignition source), fires in plant to recover acetone from air with active carbon are due to the bulk surface effect of oxidative heating when air flow is too low to cool effectively.

Chloroform

See Chloroform: Acetone, etc.

2-Methyl-1,3-butadiene

See 2-Methyl-1,3-butadiene: Acetone

Nitric acid, Sulfuric acid MRH Nitric 5.86/77, Sulfuric 1.05/53

Fawcett, H. H., *Ind. Eng. Chem.*, 1959, **51**(4), 89A

Acetone will be oxidised with explosive violence if brought into contact with the mixed (nitrating) acids, particularly under confinement.

See Oxidants, below

Other reactants

Yoshida, 1980, 20

MRH values calculated for 17 combinations with oxidants are given.

Oxidants MRH values show % of oxidant

See Nitric acid, Sulfuric acid, above
Bromine trifluoride: Solvents
Bromine: Acetone

Chromium trioxide: Acetone	MRH 2.59/90
Chromyl chloride: Organic solvents	
Dioxygen difluoride: Various materials	
Hydrogen peroxide: Acetone	MRH 6.36/81
Hydrogen peroxide: Ketones, or: Oxygenated compounds	
Nitric acid: Acetone	MRH 5.86/77
Nitrosyl chloride: Acetone, etc.	
Nitrosyl perchlorate: Organic materials	
Oxygen (Gas): Acetylene, Acetone	
Peroxomonosulfuric acid: Acetone	

Peroxyacetic acid
See 5-Bromo-4-pyrimidinone

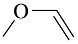
Phosphoryl chloride
See Phosphoryl chloride: Acetone

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

Sulfur dichloride
See Sulfur dichloride: Acetone

Thiotrithiazyl perchlorate
See Thiotrithiazyl perchlorate: Organic solvents

†1217. Methyl vinyl ether (Methoxyethene)
[107-25-5] **C_3H_6O**



HCS 1980, 664 (cylinder)

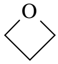
Acids

1. Braker, 1980, 487
2. ‘MVE’ Brochure, Billingham, ICI, 1962

Methyl vinyl ether is rapidly hydrolysed by contact with dilute acids to form acetaldehyde, which is more reactive and has wider flammability limits than the ether [1]. Presence of base is essential during storage or distillation of the ether to prevent rapid acid-catalysed homopolymerisation, which is not prevented by antioxidants. Even mildly acidic solids (calcium chloride or some ceramics) will initiate exothermic polymerisation [2].
See other POLYMERISATION INCIDENTS

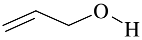
Halogens, or Hydrogen halides
Braker, 1980, 487
Addition reactions with bromine, chlorine, hydrogen bromide or hydrogen chloride are very vigorous and may be explosive if uncontrolled.
See other PEROXIDISABLE COMPOUNDS

†1218. Oxetane
[503-30-0] **C_3H_6O**



Dinitrogen pentaoxide
See Dinitrogen pentaoxide: Strained ring heterocycles
See other STRAINED-RING COMPOUNDS

†1219. 2-Propen-1-ol (Allyl alcohol)
[107-18-6] **C_3H_6O**



HCS 1980, 122

Energy of decomposition (in range 360—500°C) measured as 0.69 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkali, 2,4,6-Trichloro-1,3,5-triazine MRH Sodium hydroxide 1.21/tr.
See 2,4,6-Trichloro-1,3,5-triazine: Allyl alcohol, etc.

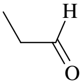
Carbon tetrachloride MRH 1.42/73
491M, 1975, 21
Interaction gives an unstable mixture of halogenated C_4 epoxides which exploded during distillation.

Other reactants
Yoshida, 1980, 24
MRH values calculated for 15 combinations, mainly with oxidants, are given.

Sulfuric acid MRH 1.42/53
Senderens, J. B., *Compt. rend.*, 1925, **181**, 698—700
During preparation of diallyl ether by dehydration of the alcohol with sulfuric acid, a violent explosion may occur (possibly involving peroxidation and certainly polymerisation).
See other PEROXIDATION INCIDENTS, POLYMERISATION INCIDENTS

2,4,6-Tris(bromoamino)-1,3,5-triazine
See 2,4,6-Tris(bromoamino)-1,3,5-triazine: Allyl alcohol
See other ALLYL COMPOUNDS

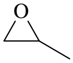
†1220. Propionaldehyde (Propanal)
[123-38-6] **C_3H_6O**



HCS 1980, 791

Methyl methacrylate
See Methyl methacrylate: Propionaldehyde
See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

†1221. Propylene oxide (Methyloxirane)
[75-56-9] **C_3H_6O**



FPA H88, 1980; *HCS 1980*, 800

1. *CHETAH*, 1990, 183
2. Kulik, M. K., *Science*, 1967, **155**, 400
3. Smith, R. S., *Science*, 1967, **156**, 12
4. Pogany, G. A., *Chem. & Ind.*, 1979, 16—21
5. *See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

The liquid can be exploded by a detonator, though not by mechanical shock [1]. Use of propylene oxide as a biological sterilant is hazardous because of ready formation of explosive mixtures with air (2.8—37%). Commercially available mixtures with carbon dioxide, though non-explosive, may be asphyxiant and vesicant [1]. Such mixtures may be ineffective, but neat propylene oxide vapour may be used safely, provided that it is removed by evacuation using a water-jet pump [2]. The main factors involved in the use and safe handling on a laboratory scale have been discussed [3]. The energy of decomposition (in range 340—500°C) has been measured as 1.114 kJ/g [4].

Epoxy resin
Sheaffer, J., *CHAS Notes*, 1981, **1**(4), 5
Mixing of propylene oxide and epoxy resin in a waste bottle led to an explosion, probably owing to the polymerisation of the oxide catalysed by the amine accelerator in the resin.
See Sodium hydroxide, below

Ethylene oxide, Polyhydric alcohol
See Ethylene oxide: Polyhydric alcohol, etc.

Other reactants
Yoshida, 1980, 322
MRH values calculated for 13 combinations with oxidants are given.

Oxygen
1. Hassan, A. *et al., Combust. Sci. Technol.*, 1983, **35**, 215—230
2. Peng, J., *Proc. Int. Pyrotech, Semin.*, 1991, (17th), Vol. 1, 353

The transition of deflagration to detonation in mixtures was studied with respect to mixing ratio, pressure and spark energy [1]. A study of TNT equivalences in propylene oxide fuel/air explosives is made [2].

Sodium hydroxide

1. *MCA Case History No. 31*
2. Freeder, B. G. *et al., J. Loss Prev. Process Ind.*, 1988, **1**, 164—168

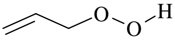
A drum of crude product containing unreacted propylene oxide and sodium hydroxide catalyst exploded and ignited, probably owing to base-catalysed exothermic polymerisation of the oxide [1]. A comparative ARC study of the runaway exothermic polymerisation of ethylene oxide and the less reactive propylene oxide in presence of sodium hydroxide solutions, as typical catalytically active impurities, has been done. The results suggest that the hazard potential for propylene oxide is rather less than that for the lower homologue, though more detailed work is needed to quantify the difference [2].

See Ethylene oxide: Contaminants

See other CATALYTIC IMPURITY INCIDENTS, 1,2-EPOXIDES, POLYMERISATION INCIDENTS

1222. Allyl hydroperoxide (2-Propenyl hydroperoxide)

[6069-42-7] **$C_3H_6O_2$**



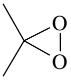
1. Dykstra, S. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 3474
2. Seyfarth, H. E. *et al., Angew. Chem.*, 1965, **77**, 1078

When impure, the material is unstable towards heat or light and decomposes to give an explosive residue. The pure material is more stable to light, but detonates on heating or in contact with solid alkalies [1]. Preparation by action of oxygen on diallylzinc gives improved yields, but there is a risk of explosion. The peroxide is also impact-sensitive if sand is admixed [2].

See other ALKYL HYDROPEROXIDES, ALLYL COMPOUNDS

1223. Dimethyldioxirane

[74087-85-7] **$C_3H_6O_2$**



Murray, R. W., private communication, 1992

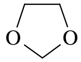
This material, and homologues, are being recommended as oxidants, they are prepared in situ and very dilute. Thus far, the material has shown itself surprisingly stable during isolation and pyrolysis (decomposes slowly at ambient temperatures and quietly on heating) and even explosivity testing [1]. However several known oligomers, presumably of lower (strain) energy, are dangerously sensitive explosives. Considerable caution during work-up of reactions is recommended.

See Bis(trifluoromethyl)dioxirane

See Hydrogen Peroxide: Acetone

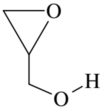
See other CYCLIC PEROXIDES

†1224. 1,3-Dioxolane
[646-06-0] **$C_3H_6O_2$**



Lithium perchlorate
See Lithium perchlorate: 1.3-Dioxolane

1225. 2,3-Epoxypropanol (Oxiranemethanol)
[556-52-5] **$C_3H_6O_2$**



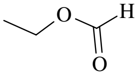
HCS 1980, 518

1. Anon., *Jahresber.*, 1982, 67—68; *Sichere Chemiearb.*, 1984, **36**, 80
2. Anon, *Loss Prevention Bull.*, 1989, **88**, 17
3. Cardillo, P. *et al., J. Loss Prev. Process Ind.*, 1991, **4**(4), 242

Off-specification ‘glycidol’ from a production unit was collected in a 40 t storage tank and recovered occasionally by redistillation. As no stabiliser is known, the contents were water-cooled to prevent self-heating and polymerisation, and pump-circulated to ensure homogeneity. A 9 t quantity of the stored material was found to be quite warm, and soon after, the tank exploded, causing 3 fatalities. The contents of the tank had been subjected to storage tests at 60°C on 200 l scale, when decomposition but no runaway was seen, presumably the drums were not adiabatic enough. It is known that the epoxy compound will undergo explosive decomposition in presence of strong acids or bases, salts (aluminium chloride, iron(III) chloride, tin(IV) chloride), or metals (copper or zinc), but these were not likely to have been present. It was concluded that the water cooling had been turned off, and that the energy dissipated by the circulation pump would have raised the temperature of the tank contents to 50°C under the prevailing weather conditions, the latter conclusion being confirmed experimentally [1]. The energy of decomposition (in the range 130—450°C) has been measured by DSC as 1.365 kJ/g, and T_{ait24} was determined as the low figure of 65°C by adiabatic Dewar tests, with an apparent energy of activation of 71 kJ/mol. A detailed study of the thermochemistry of glycidol, including CHETAH calculations and calorimetry (ARC and DSC), showed a two stage reaction; polymerisation from 60°C, followed by a decomposition with pressure generation from 280°C. Polymerisation was catalysed by NaOH and triethanolamine but not, apparently, by HCl or triethylamine [3].

See also CALORIMETRY; COMPUTATION OF REACTIVE CHEMICAL HAZARDS
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION
See other 1,2-EPOXIDES

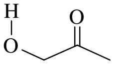
†1226. Ethyl formate (Ethyl methanoate)
[109-94-4] **$C_3H_6O_2$**



HCS 1980, 488

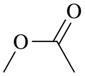
Base
See Methyl formate: Methanol, Sodium methoxide

1227. Hydroxyacetone (Propan-1-ol-2-one)
[116-09-6] **$C_3H_6O_2$**



Preparative hazard
See 3-Propynol: Mercury(II) sulfate, etc.

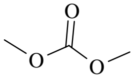
†1228. Methyl acetate (Methyl ethanoate)
[79-20-9] **$C_3H_6O_2$**



FPA H124, 1983; *HCS 1980*, 426

Other reactants
Yoshida, 1980, 123
MRH values calculated for 13 combinations with oxidants are given.

†1229. Dimethyl carbonate
[616-38-6] **$C_3H_6O_3$**

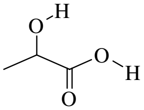


HCS 1980, 426

Other reactants
Yoshida, 1980, 224
MRH values calculated for 13 combinations with oxidants are given.

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

1230. Lactic acid (2-Hydroxypropanoic acid)
[598-82-3] $C_3H_6O_3$

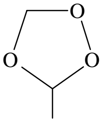


Hydrofluoric acid, Nitric acid

See Nitric acid: Hydrofluoric acid, Lactic acid

See other ORGANIC ACIDS

1231. 3-Methyl-1,2,4-trioxolane (Propene ozonide)
[38787-96-1] $C_3H_6O_3$

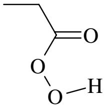


Briner, E. *et al., Helv. Chim. Acta*, 1929, **12**, 181

Stable at 0°C but often explosively decomposes at ambient temperature.

See other CYCLIC PEROXIDES, OZONIDES

1232. Peroxypropionic acid (Propaneperoxoic acid)
[4212-43-5] $C_3H_6O_3$



1. Swern, D., *Chem. Rev.*, 1949, **45**, 9
2. Phillips, B. *et al., J. Org. Chem.*, 1959, **23**, 1823

More stable than its lower homologues, it merely deflagrates on heating. Higher homologues appear to be still more stable [1]. Safe procedures (on the basis of detonability experiments) for preparation of anhydrous solutions of peroxypropionic acid in chloroform or ethyl propionate have been described [2].

Organic solvents

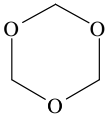
Manly, T. D., *Chem. Brit.*, 1982, **18**, 341

A violent explosion occurred during the distillation of solvents that had contained the peroxyacid. Although the solvents had been treated by addition of sodium sulfite to reduce the acid, dipropionyl peroxide (which is not reduced by sulfite, and which may have been produced by the sulfite treatment) remained in solution and subsequently decomposed on heating. If the solvent is added to the sulfite solution, the diacyl peroxide is not formed.

See DIACYL PEROXIDES

See other PEROXYACIDS

1234a. 1,3,5-Trioxane
[110-88-3] **$C_3H_6O_3$**



HCS 1980, 942
MCA Case History No. 1129

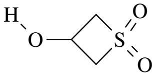
Use of an axe to break up a large lump of trioxane caused ignition and a vigorous fire. Peroxides may have been involved.

Acrylonitrile
See Acrylonitrile: Formaldehyde

Hydrogen peroxide, Lead
See Hydrogen peroxide: Lead, Trioxane

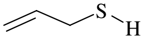
Oxygen (Liquid)
See Oxygen (Liquid): 1,3,5-Trioxane
See PEROXIDISABLE COMPOUNDS

1234b. 3-Thietanol-1,1-dioxide
[22524-35-2] **$C_3H_6O_3S$**



Preparative hazard
See Hydrogen peroxide: Acetic acid, 3-Thietanol

†1235a. 2-Propene-1-thiol (Allyl mercaptan)
[870-23-5] **C_3H_6S**



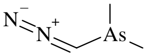
See other ALLYL COMPOUNDS

†1235b. 2-Propynylstannane (Propargylstannane)
[254995-81-8] **C_3H_6Sn**

$HC{\equiv}CCH_2SnH_3$

Guillemin, J-C. *et al., Organometallics*, 1999, **18**(25), 5259
See other ACETYLENIC COMPOUNDS, ALKYLMETAL HYDRIDES

1236. Diazomethyldimethylarsine
[59871-26-0] **$C_3H_7AsN_2$**

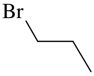


Preparative hazard

See Diazomethane: Dimethylaminodimethylarsine

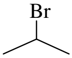
See other DIAZO COMPOUNDS

†1237. 1-Bromopropane (Propyl bromide)
[106-94-5] **C_3H_7Br**



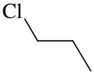
See other HALOALKANES

†1238. 2-Bromopropane (Isopropyl bromide)
[75-26-3] **C_3H_7Br**



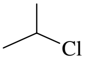
See other HALOALKANES

†1239. 1-Chloropropane (Propyl chloride)
[540-54-5] **C_3H_7Cl**



See other HALOALKANES

†1240. 2-Chloropropane (Isopropyl chloride)
[75-29-6] **C_3H_7Cl**

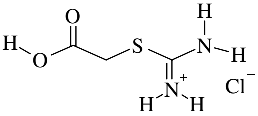


HCS 1980, 578

See other HALOALKANES

1241. *S*-Carboxymethylisothiouronium chloride (Carboxymethyl carbamimoniothioate chloride)

[5425-78-5] **$C_3H_7ClN_2O_2S$**



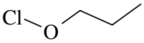
Chlorine

See Chlorine: Nitrogen compounds (reference 4)

See related ORGANIC ACIDS

†1242. Chloromethyl ethyl ether (Chloromethoxyethane)

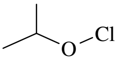
[3188-13-4] **C_3H_7ClO**



See related HALOALKANES

1243. Isopropyl hypochlorite

[53578-07-7] **C_3H_7ClO**



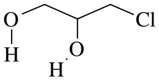
1. Chattaway, F. D. *et al., J. Chem. Soc.*, 1923, **123**, 3001
2. Mellor, 1956, Vol. 2, Suppl. 1, 550

Of extremely low stability; explosions occurred during its preparation if cooling was inadequate [1], or on exposure to light [2].

See other HYPOHALITES, IRRADIATION DECOMPOSITION INCIDENTS

1244. 3-Chloro-1,2-propanediol

[96-24-2] **$C_3H_7ClO_2$**

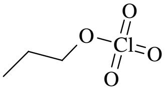


Perchloric acid

See Perchloric acid: Glycols, etc. (reference 1)

1245. Propyl perchlorate

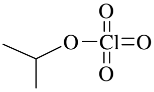
[22755-14-2] **$C_3H_7ClO_4$**



See entry ALKYL PERCHLORATES

1246. 2-Propyl perchlorate

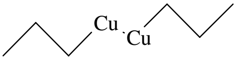
[52936-33-1] **$C_3H_7ClO_4$**



See entry ALKYL PERCHLORATES (reference 6)

1247. Propylcopper(I)

[18365-12-3] **C_3H_7Cu**



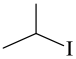
Houben-Weyl 1970, Vol. 13.1, 737

Small quantities only should be handled because of the danger of explosion.

See other ALKYLMETALS

†1248. 2-Iodopropane (Isopropyl iodide)

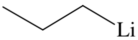
[75-30-9] **C_3H_7I**



See other HALOALKANES, IODINE COMPOUNDS

1249. Propyllithium

[2417-93-8] **C_3H_7Li**



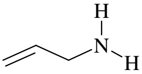
Leleu, *Cahiers*, 1977, (88), 368

It ignites in air.

See other ALKYLMETALS

†1250. 3-Aminopropene (Allylamine)

[107-11-9] **C_3H_7N**

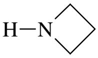


HCS 1980, 123

See other ALLYL COMPOUNDS

†1251. Azetidine

[503-29-7] **C_3H_7N**



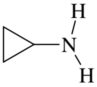
Dinitrogen pentaoxide

See Dinitrogen pentaoxide: Strained ring heterocycles

See other STRAINED-RING COMPOUNDS

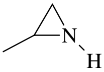
†1252. Cyclopropylamine

[765-30-0] **C_3H_7N**



†1253. 2-Methylaziridine (Propyleneimine)

[75-55-8] **C_3H_7N**



Acids

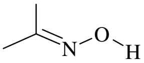
Inlow, R. O. *et al., J. Inorg. Nucl. Chem.*, 1975, **37**, 2353

Like the lower homologue ethyleneimine, it may polymerise explosively if exposed to acids or acidic fumes, so it must always be stored over solid alkali.

See other POLYMERISATION INCIDENTS

1254. Acetone oxime (2-Hydroxyiminopropane)

[127-06-0] **C_3H_7NO**



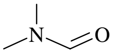
Energy of decomposition (in range 200—420°C) measured as 1.5 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other OXIMES

1255. Dimethylformamide

[68-12-2] **C_3H_7NO**



HCS 1980, 430; *RSC Lab. Hazard Data Sheet No.17*, 1983

This powerful aprotic solvent is not inert and reacts vigorously or violently with a range of materials.

See *endo*-2,5-Dichloro-7-thiabicyclo[2.2.1]heptane: Dimethylformamide
Diisocyanatomethane: Dimethylformamide
Lithium azide: Alkyl nitrates, etc.
Sodium hydride: Dimethylformamide
Sodium tetrahydroborate: Dimethylformamide
Sodium: Dimethylformamide
Sulfinyl chloride: Dimethylformamide
Tetraphosphorus decaoxide: Organic liquids
2,4,6-Trichloro-1,3,5-triazine: Dimethylformamide
Triethylaluminium: Dimethylformamide

Allyl trifluoromethanesulfonates
See ALLYL TRIFLUOROMETHANESULFONATES: Alone, or Aprotic solvents

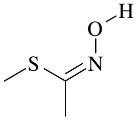
3-Chloroperoxybenzoic acid
See 3-Chloroperoxybenzoic acid

Halocarbons
1,2,3,4,5,6-Hexachlorocyclohexane: Dimethylformamide
See Carbon tetrachloride: Dimethylformamide
See *N,N*-Dimethylacetamide: Halogenated compounds, etc.
See other CATALYTIC IMPURITY INCIDENTS

Other reactants
Yoshida, 1980, 172
MRH values calculated for 13 combinations with oxidants are given.

Oxidants
Pal, B. C. *et al., Chem. Eng. News*, 1981, **59**(17), 47
Explosions involving chromium trioxide or potassium permanganate and dimethylformamide are explained in terms of DMF being, like formic acid, a reducing agent. Dimethylacetamide is recommended as a safer, less reducing substitute solvent for DMF. For other combinations listed
See Bromine: Dimethylformamide
Chlorine: Dimethylformamide
Chromium trioxide: Dimethylformamide
Magnesium nitrate: Dimethylformamide
Potassium permanganate: Dimethylformamide
Uronium perchlorate: Organic materials
See other APROTIC SOLVENTS

1256. *S*-Methylthioacetohydroximate
[13749-94-5] **C_3H_7NOS**

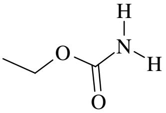


Preparative hazard

Oren, Z. *et al., Israeli Patent IL 89641*, 1995; *Chem. Abs.*, 1996, **124**, 260401g

It is claimed that a prior method of manufacture from acetonitrile, methanethiol and hydroxylamine hydrochloride gave uncontrolled reaction and explosion. A safer preparation starting from acetaldoxime is claimed.

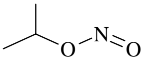
1257. Ethyl carbamate
[51-79-6] **$C_3H_7NO_2$**



Phosphorus pentachloride

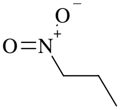
See N-Carbomethoxyiminophosphoryl chloride

†1258. Isopropyl nitrite
[541-42-4] **$C_3H_7NO_2$**



See other ALKYL NITRITES

1259. 1-Nitropropane
[108-03-2] **$C_3H_7NO_2$**



Metal oxides

See other NITROALKANES: Metal oxides

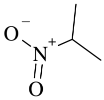
Other reactants

Yoshida, 1980, 276

MRH values calculated for 14 combinations, mainly with oxidants, are given.

See other NITROALKANES

1260. 2-Nitropropane
[79-46-9] **$C_3H_7NO_2$**



HCS 1980, 689; *RSC Lab. Hazard Data Sheet No.10*, 1983

Amines, Heavy metal oxides

'Tech Data Sheet No. 7', New York, Comml. Solvents Corp., 1968

Contact with amines and mercury oxide or silver oxide may lead to formation of unstable salts analogous to those of nitromethane.

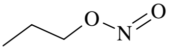
See other NITROALKANES

Carbon, Hopcalite

'Tech. Data Sheet No. 7', New York, Comml. Solvents Corp., 1968

The heat of adsorption of 2-nitropropane is very high, so carbon-containing respirators should not be used in high vapour concentrations. Also, if Hopcalite catalyst (co-precipitated copper(II) oxide and manganese (IV) oxide) is present in the respirator cartridge, ignition may occur.

†1261. Propyl nitrite
[543-67-9] **$C_3H_7NO_2$**

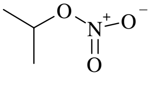


Anon., private comm., 1985

Bottles of isopropyl nitrite decomposed during refrigerated storage, developing enough internal pressure to burst the containers and blow open the refrigerator door. Other alkyl nitrites lower than amyl nitrite may be expected to behave similarly.

See other ALKYL NITRITES

†1262. Isopropyl nitrate
[1712-64-7] **$C_3H_7NO_3$**



1. 'Tech. Bull. No. 2', London, ICI Ltd., 1964
2. Brochet, C., *Astronaut. Acta*, 1970, **15**, 419—425
3. Beeley, P. *et al., Chem. Abs.*, 1977, **87**, 120000
4. Beeley, P. *et al., Comb. Flame*, 1980, **39**, 255—268, 269—281

The self-sustaining exothermic decomposition/combustion characteristics of this fuel of negative oxygen balance (—68%) renders it suitable as a rocket monopropellant.

Storage and handling precautions are detailed [1]. Conditions for detonation of the nitrate, an explosive of low sensitivity, have been investigated [2]. The pure vapour ignites spontaneously at very low temperatures and pressures, and other aspects were studied in detail [3], including spontaneous ignition on compression [4].

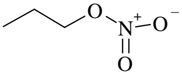
Lewis acids

See ALKYL NITRATES: Lewis acids

See other ALKYL NITRATES

†1263. Propyl nitrate

[627-13-4] **$C_3H_7NO_3$**



Other reactants

Yoshida, 1980, 204

MRH Values calculated for 11 combinations are given.

Solvents

Breslow, B. A., US Pat. 4 042 032, 1977

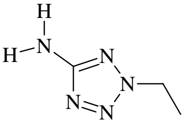
The shock-sensitive nitrate is desensitised by 1—2% of propane, butane, chloroform, dimethyl ether or diethyl ether.

See THERMAL EXPLOSIONS

See other ALKYL NITRATES

1264. 5-Amino-2-ethyl-2*H*-tetrazole

[95112-14-4] **$C_3H_7N_5$**



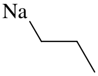
Aluminium hydride

See Aluminium hydride: Tetrazole derivatives

See other TETRAZOLES

1265. Propylsodium

[15790-54-2] **C_3H_7Na**



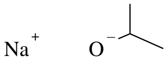
Houben-Weyl, 1970, Vol. 13.1, 384

The powder ignites in air.

See other ALKYLMETALS

1266. Sodium isopropoxide

[683-60-3] **C_3H_7NaO**



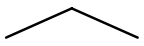
Dimethyl sulfoxide

See Dimethyl sulfoxide: Metal alkoxides

See other METAL ALKOXIDES

†1267. Propane

[74-98-6] **C_3H_8**



FPA H10, 1973 (cylinder); *HCS 1980*, 780 (cylinder)

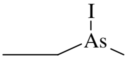
Barium peroxide

See Barium peroxide: Propane

See also CRYOGENIC LIQUIDS (reference 10), LIQUEFIED PETROLEUM GASES

1268. Ethyliodomethylarsine

[65313-31-7] **C_3H_8AsI**



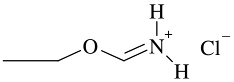
Leleu, *Cahiers*, 1977, (88), 363

It ignites in air.

See other ALKYLNON-METAL HALIDES

1269. Ethyl iminioformate chloride

[16694-46-5] **C_3H_8ClNO**

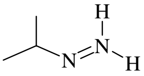


Preparative hazard

See Hydrogen chloride: Alcohols, Hydrogen cyanide

1270. Isopropyldiazene

[26981-95-3] **$C_3H_8N_2$**



Chlorine

Abendroth, H. J., *Angew. Chem.*, 1959, **71**, 340

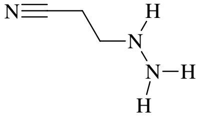
The crude chlorination product of 'isoacetone hydrazone' (presumably an *N*-chloro compound) exploded violently during drying at 0°C.

See *N*-HALOGEN COMPOUNDS

See related AZO COMPOUNDS

1271. 3-Hydrazinopropanenitrile (3-Cyanoethylhydrazine)

[353-07-1] **$C_3H_7N_3$**



Jasiewicz, M. L., *Chem. & Ind.*, 1996, (3), 70

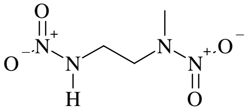
In the late stage of work up of a sample prepared from acrylonitrile and hydrazine hydrate and stripped of water by a procedure involving dichloromethane, the distillation flask pressurised and burst, shattering the front of the fume cupboard. Previously, slight pressurisation had once been observed. Involving both a nitrile and a hydrazino moiety, this molecule cannot be thermodynamically stable but it has not given previous problems.

See Dichloromethane: 1,2-Diaminoethane, 3-Aminopropionitrile

See CYANO COMPOUNDS

1272. *N,N′*-Dinitro-*N*-methyl-1,2-diaminoethane

[10308-90-4] **$C_3H_8N_4O_4$**



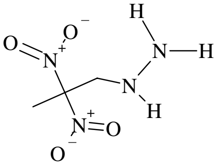
Violent decomposition occurred at 210°C.

See entry DIFFERENTIAL THERMAL ANALYSIS (reference 1)

See other N—NITRO COMPOUNDS

1273. 2,2-Dinitropropylhydrazine

[ ] **$C_3H_8N_4O_4$**



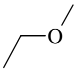
Borane

See Borane bis(2,2-dinitropropylhydrazine)

See other POLYNITROALKYL COMPOUNDS

†1274. Ethyl methyl ether (Methoxyethane)

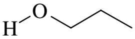
[540-67-0] **C_3H_8O**



HCS 1980, 498

†1275. Propanol (1-Hydroxypropane)

[71-23-8] **C_3H_8O**



HCS 1980, 797

Other reactants

Yoshida, 1980, 315

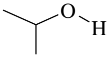
MRH values calculated for 13 combinations with oxidants are given.

Potassium *tert*-butoxide

See Potassium *tert*-butoxide: Acids, etc.

†1276. 2-Propanol (Isopropanol)

[67-63-0] **C_3H_8O**



(*MCA SD-98*, 1972); *FPA H45*, 1976; *HCS 1980*, 783

1. Renfrew, M. M., *J. Chem. Educ.*, 1983, **60**(9), A229
2. Bonafede, J. D., *J. Chem. Educ.*, 1984, **61**, 632
3. Redemann, C. E., *J. Amer. Chem. Soc.*, 1942, **64**, 3049
4. Mirafzal, G. A. *et al., J. Chem. Educ.*, 1988, **65**(9), A226—229
5. Bohanon, J. T., *Chem. Eng. News*, 1989, **67**(1), 4

Several explosions have occurred during laboratory distillation of isopropanol [1,2,4,5], some with a sample stored for 5 years in a part empty can [5]. No cause was apparent, but presence of traces of ketone(s) promoting peroxidation is a probability. Previously, the presence of 0.36M peroxide had been reported in a 99.5% pure sample of isopropanol stored for several months in a partially full clear glass bottle in strong daylight [3]. The reformation of peroxides in de-peroxided isopropanol 'within a few days' had been noted [2]. It appears that the tertiary H on the 2-position is susceptible to autoxidation, and that 2-propanol must be classed as peroxidisable.

2-Hydroperoxy-2-hydroxypropane has, in fact, been isolated from photocatalysed oxidation of isopropanol.
See 2-Butanone, below
See also Oxygen (Gas): Alcohols
See PEROXIDISABLE COMPOUNDS (reference 7)

Aluminium
See Aluminium: 2-Propanol

Aluminium isopropoxide, Crotonaldehyde
Wagner-Jauregg, T., *Angew. Chem.*, 1939, **53**, 710
During distillation of 2-propanol recovered from the reduction of crotonaldehyde with isopropanol/aluminium isopropoxide, a violent explosion occurred. This was attributed to peroxidised diisopropyl ether (a possible by-product) or to peroxidised crotonaldehyde. An alternative or additional possibility is that the isopropanol may have contained traces of a higher secondary alcohol (e.g. 2-butanol) which would be oxidised during the Meerwein-Ponndorf reduction procedure to 2-butanone. The latter would then effectively sensitise the isopropanol or other peroxidisable species to peroxidation.
See 2-Butanone, next below
See also Diisopropyl ether

2-Butanone
1. Bathie, H. M., *Chem. Brit.*, 1974, **10**, 143
2. Unpublished observations, 1974
3. Pitt, M. J., *Chem. Brit.*, 1974, **10**, 312
4. Schenk, G. O. *et al., Angew. Chem.*, 1958, **70**, 504

Distillation to small volume of a small sample of a 4-year-old mixture of the alcohol with 0.5% of the ketone led to a violent explosion, and the presence of peroxides was subsequently confirmed [1]. Pure alcohols which can form stable radicals (secondary branched structures) may slowly peroxidise to a limited extent under normal storage conditions (isopropanol to 0.0015M in brown bottle, subdued light during 6 months; to 0.0009M in dark during 5 years) [2]. The presence of ketones markedly increases the possibility of peroxidation by sensitising photochemical oxidation of the alcohol. Acetone (produced during autoxidation of isopropanol) is not a good sensitiser, but the presence of even traces of 2-butanone in isopropanol would be expected to accelerate markedly peroxidation of the latter. Treatment of any mixture or old sample of a secondary alcohol with tin(II) chloride and then lime before distillation is recommended [3]. The product of photosensitised oxidation is 2-hydroperoxy-2-propanol [4].
See 2-Butanol

Hydrogen peroxide
Baratov, A. N. *et al., Chem. Abs.*, 1978, **88**, 39537
Addition of a small amount of hydrogen peroxide may reduce sharply the AIT of the alcohol (455°C), probably to that of the hydroperoxide.

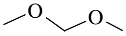
Other reactants
Yoshida, 198, 41

MRH values calculated for 13 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Barium perchlorate: Alcohols	
Chromium trioxide: Alcohols	MRH 2.47/91
Dioxygenyl tetrafluoroborate: Organic materials	
Hydrogen peroxide: Oxygenated compounds	MRH 6.32/84
Oxygen (Gas): Alcohols	
Sodium dichromate: 2-Propanol, etc.	
Trinitromethane: 2-Propanol	

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

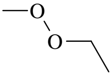
†1277. Dimethoxymethane
[109-87-5] **$C_3H_8O_2$**



HCS 1980, 419

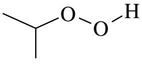
Oxygen
Molem, M. J. *et al., Chem. Abs.*, 1975, **83**, 45495
The nature of the reaction and the products in methylal—oxygen mixtures during cool flame or explosive oxidation were studied.
See other PEROXIDISABLE COMPOUNDS

1278. Ethyl methyl peroxide
[70299-48-8] **$C_3H_8O_2$**



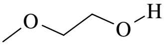
Rieche, A., *Ber.*, 1929, **62**, 218
Shock-sensitive as a liquid or vapour, it explodes violently on superheating.
See other DIALKYL PEROXIDES

1279. Isopropyl hydroperoxide (2-Hydroperoxypropane)
[3031-75-2] **$C_3H_8O_2$**



Medvedev, S. *et al., Ber.*, 1932, **65**, 133
It explodes just above the b.p., 107—109°C.
See other ALKYL HYDROPEROXIDES

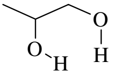
1280. 2-Methoxyethanol (Ethylene glycol monomethyl ether)
[109-86-4] **$C_3H_8O_2$**



HCS 1980, 799

491M, 1975, 256
It forms explosive peroxides.
See other PEROXIDISABLE COMPOUNDS

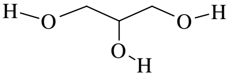
1281. Propylene glycol (1,2-Propanediol)
[57-55-6] **$C_3H_8O_2$**



HCS 1980, 782

Hydrofluoric acid, Nitric acid, Silver nitrate
See Nitric acid: Hydrofluoric acid, Propylene glycol, etc.

1282. Glycerol (1,2,3-Propanetriol)
[56-81-5] **$C_3H_8O_3$**



HCS 1980, 516

Ethylene oxide
See Ethylene oxide: Glycerol

Other reactants
Yoshida 1980, 448
MRH values calculated for 16 combinations, mainly with oxidants, are given.

Oxidants MRH values show % of oxidant
Unpublished comments, 1978
The violent or explosive reactions exhibited by glycerol in contact with many solid oxidants are due to its unique properties of having three centres of reactivity, of being a liquid which ensures good contact, and of high boiling point and viscosity which prevents dissipation of oxidative heat. The difunctional, less viscous liquid glycols show similar but less extreme behaviour.
See Calcium hypochlorite: Hydroxy compounds MRH 2.13/88
Chlorine: Glycerol
Hydrogen peroxide: Organic compounds (reference 2) MRH 5.56/71
Nitric acid: Glycerol

  Nitric acid: Glycerol, Hydrochloric acid
  Nitric acid: Glycerol, Hydrofluoric acid
  Perchloric acid, Glycerol, etc. MRH Nitric 4.89/65, Sulfuric 0.9/26
  Potassium permanganate MRH 2.76/85
  Sodium peroxide: Hydroxy compounds MRH 2.72/85

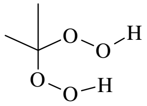
Phosphorus triiodide
See Phosphorus triiodide: Hydroxylic compounds

Sodium hydride
See Sodium hydride: Glycerol

Sodium tetrahydroborate
See Sodium tetrahydroborate: Glycerol

1283. 2,2-Bis(hydroperoxy)propane

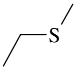
[2614-76-8] **$C_3H_8O_4$**



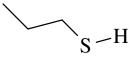
1. Hutton, W. *et al., Chem. Eng. News*, 1984, **62**(38), 4
2. Sauer, M. C. V., *J. Phys. Chem.*, 1972, **76**, 1283—1288
3. Hutton, W., *private comm.*, 1984
4. Schwoegler, E. J., *Chem. Eng. News*, 1985, **63**(1), 6
5. Bodner, G. M., J. *Chem. Educ.*, 1985, **62**, 1105

The thermal instability of the bis-hydroperoxide ('peroxyacetone') has long been recognised and used in demonstrations of the violent combustion of peroxides. In thin layers a fireball is produced, while ignition of lumps or samples confined in a deflagrating spoon was likely to produce detonation. The compound had been used several times for such demonstrations without indication of undue sensitivity to shock or normal careful handling procedures. When one sample, stored in an open jar for 48 hours, was being sprinkled from it as usual for disposal by burning, it detonated violently [1]. Though exposure to acid fumes might have led to formation of the extremely sensitive trimeric acetone peroxide [2], no such exposure was likely. It was concluded that the peroxide may have become unusually dry and sensitive during its exposure to atmosphere in a hood, and that it should no longer be used for such demonstrations. [3]. Hutton's interpretation is incorrect, because 2,2-dihydroperoxypropane is not a solid, but a liquid. Most probably the material was the solid trimeric acetone peroxide [4]. Several other incidents, usually involving injury, are described [5].
See 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane

†1284. Ethyl methyl sulfide
[624-89-5] **C_3H_8S**

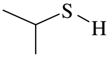


†1285. Propanethiol
[107-03-9] **C_3H_8S**



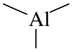
Calcium hypochlorite
See Calcium hypochlorite: Organic sulfur compounds
See other ALKANETHIOLS

†1286. 2-Propanethiol
[75-33-2] **C_3H_8S**



See other ALKANETHIOLS

1287. Trimethylaluminium
[75-24-1] **C_3H_9Al**



HCS 1980, 938

Kirk-Othmer 1963, Vol. 2, 40
Extremely pyrophoric, ignition delay 13 ms in air at 235°C/0.16 bar.

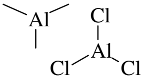
Dichlorodi-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium
See Dichlorodi-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium: Air, Alkylmetals

Other reactants
Yoshida, 1980, 257
MRH values calculated for 15 combinations, largely with oxidants, are given.

Tetrafluorobenzene-1,4-diol
Spence, R., *Chem. Eng. News*, 1996, **74**(21), 4
The dried product of reaction of approximately equimolar quantities of the diol and methyl aluminium exploded when crushed with a spatula.
See METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

See entry TRIALKYLALUMINIUMS
See other ALKYLMETALS

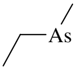
1288. Trimethyldialuminium trichloride (Aluminium chloride—trimethylaluminium complex)
[12542-85-7] **$C_3H_9Al_2Cl_3$**



HCS 1980, 636

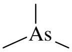
See entry ALKYLALUMINIUM HALIDES

1289. Ethylmethylarsine
[689-93-0] **C_3H_9As**



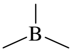
Leleu, *Cahiers*, 1977, (88), 362
It ignites in air.
See other ALKYLNON-METAL HYDRIDES

1290. Trimethylarsine
[593-88-4] **C_3H_9As**



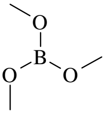
Air, or Halogens
Sidgwick, 1950, 762, 769
It inflames in air, and interaction with halogens is violent.
See other ALKYLNON-METALS

1291. Trimethylborane
[593-90-8] **C_3H_9B**



Stock, A. *et al., Ber.*, 1921, **54**, 535
The gas ignites in air.
See Chlorine: Trialkylboranes
See other ALKYLBORANES

†1292. Trimethyl borate
[121-43-7] **$C_3H_9BO_3$**



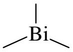
1293. 2-(Tricarbonylferra)hexaborane(10)
[75952-58-8] **$C_3H_9B_5FeO_3$**

See Structure

Preparative hazard

See Pentaborane(9): Pentacarbonyliron, Pyrex glass

1294. Trimethylbismuthine
[593-91-9] **C_3H_9Bi**



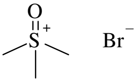
1. Coates, 1967, Vol. 1, 536
2. Sorbe, 1968, 157

It ignites in air, but is unreactive with water [1], and explodes at 110°C [2].

See TRIALKYLBISMUTHS

See other ALKYLMETALS

1295. Trimethylsulfoxonium bromide
[25596-24-1] **C_3H_9BrOS**

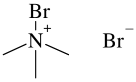


1. Scaros, M. G. *et al., Chem. Brit.*, 1973, **9**, 523; *private comm.*, 1974
2. Scaros, M. G. *et al., Proc. 7th Conf. Catal. Org. Synth. 1978*, 1980, 301—309
3. Dryden, H. L. *et al.*, US Pat. 4 141 920, 1979

Preparation of the title compound by interaction of dimethyl sulfoxide and bromomethane, sealed into a resin-coated glass bottle and heated at 65°C, led to an explosion after 120 h. The isolated salt thermally decomposes above 180°C to produce formaldehyde and a residue of methanesulfonic acid. In solution in dimethyl sulfoxide, the salt begins to decompose after several hours at 74—80°C (after exposure to light), the exothermic reaction accelerating with vigorous evolution of vapour (including formaldehyde and dimethyl sulfide), the residue of methanesulfonic acid finally attaining 132°C. Some white solid, probably poly-formaldehyde, is also produced. The explosion

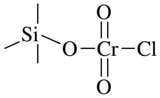
seems likely to have been a pressure-burst of the container under excessive internal pressure from the decomposition products. A safe procedure has been developed in which maximum reaction temperatures and times of 65°C and 55 h are used. Once prepared, the salt should not be redissolved in dimethyl sulfoxide. In contrast, trimethylsulfoxonium iodide appears simply to dissolve on heating rather than decomposing like the bromide [1]. The decomposition mechanism involves isomerisation of some of the product to dimethylmethoxysulfonium bromide, which then degrades to formaldehyde, dimethyl sulfide and hydrogen bromide, and the latter catalyses further decomposition reactions [2]. Use of orthoformate or orthocarbonate esters as bromine and hydrogen bromide scavengers, and a cooling/pressure venting system avoids the possibility of exothermic decomposition of the reaction mixture [3].
See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS

1296. *N*-Bromotrimethylammonium bromide(?)
[ ] **$C_3H_9Br_2N$**



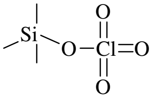
See Bromine: Trimethylamine
See other *N*-HALOGEN COMPOUNDS

1297. Trimethylsilyl chlorochromate
[102488-24-4] **$C_3H_9ClCrO_3Si$**



Aizpurna, J. M. *et al., Tetrahedron Lett.*, 1983, **24**, 4367
The oxidant appears safe when prepared and used in dichloromethane solution, but attempted isolation by distillation led to a violent explosion.
See other OXIDANTS

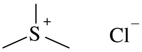
1298. Trimethylsilyl perchlorate
[18204-79-0] **$C_3H_9ClO_4Si$**



See entry ORGANOSILYL PERCHLORATES
See other NON-METAL PERCHLORATES

1299. Trimethylsulfonium chloride

[3086-29-1] **C_3H_9ClS**



Preparative hazard

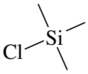
Byrne, B. *et al., Tetrahedron Lett.*, 1986, **27**, 1233—1236

During its preparation by heating dimethyl sulfide and methyl chloroformate in a glass pressure bottle at 80°C, it is essential to interrupt the reaction after 4 h, cool and release the internal pressure of carbon dioxide, before recapping the bottle and heating for a further 22 h. This avoids the possibility of excessive pressure build-up and failure of the cap seal.

See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS

†1300a. Chlorotrimethylsilane

[75-77-4] **C_3H_9ClSi**



HCS 1980, 941

Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

Preparative hazard

See Chlorine: Antimony trichloride, Tetramethylsilane

Water

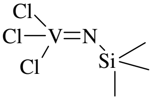
Leleu, *Cahiers*, 1977, (88), 370

It reacts violently with water.

See other ALKYLHALOSILANES

1300b. Trichloro[1,1,1-trimethylsilanaminato(2-)]vanadium

[995589-88-5] **$C_3H_9Cl_3NSiV$**



Preparative hazard

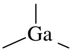
Witt, M. *et al., Inorg. Chem.*, 1997, **36**(16), 3476

If prepared from vanadium tetrachloride and trimethylsilylazide, dangerously sensitive vanadium(IV) azide trichloride appears as a byproduct. An alternative route is recommended.

See also METAL AZIDE HALIDES

1301. Trimethylgallium

[1445-79-0] **C_3H_9Ga**



Air, or Water

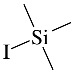
Sidgwick, 1950, 461

It ignites in air, even at —76°C, and reacts violently with water.

See other ALKYLMETALS

†1302. Iodotrimethylsilane

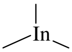
[16029-98-4] **C_3H_9ISi**



See other ALKYLHALOSILANES, IODINE COMPOUNDS

1303. Trimethylindium

[3385-78-2] **C_3H_9In**



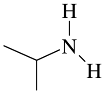
1. Bailar, 1973, Vol. 1, 1116
2. Houben-Weyl, 1970, Vol. 13.4, 351
3. Foster, D. F. *et al., Inorg. Synth.*, 1997, **31**, 29

Trimethylindium and other lower-alkyl derivatives ignite in air [1], including the 2:1 complex with diethyl ether [2]. It is reported that trimethylindium sometimes explodes during distillation [3].

See other ALKYLMETALS

†1304. Isopropylamine (2-Propanamine)

[75-31-0] **C_3H_9N**



FPA H72, 1978; *HCS 1980*, 577

1-Chloro-2,3-epoxypropane

See 1-Chloro-2,3-epoxypropane: Isopropylamine

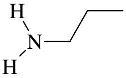
Perchloryl fluoride

See Perchloryl fluoride: Nitrogenous bases

See other ORGANIC BASES

†1305. Propylamine (Propanamine)

[107-10-8] **C_3H_9N**

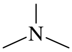


HCS 1980, 796

Triethynylaluminium
See Triethynylaluminium: Diethyl ether, etc.
See other ORGANIC BASES

†1306. Trimethylamine (*N,N*-Dimethylmethanamine)

[75-50-3] **C_3H_9N**



(*MCA SD-57*, 1955); *HCS 1980*, 939 (anhydrous), 940 (40% solution)

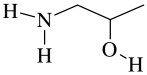
Bromine
See Bromine: Trimethylamine

Ethylene oxide MRH 3.72/100
See Ethylene oxide: Trimethylamine

Other reactants
Yoshida, 1980, 256
MRH values calculated for 14 combinations, largely with oxidants, are given.
See other ORGANIC BASES

1307. 1-Amino-2-propanol

[78-96-6] **C_3H_9NO**

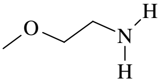


Cellulose nitrate
See CELLULOSE NITRATE: Amines

2,4-Hexadienal
See 2,4-Hexadienal: 1-Amino-2-propanol
See other ORGANIC BASES

†1308. 2-Methoxyethylamine

[109-85-3] **C_3H_9NO**



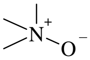
Energy of decomposition (in range 140—200°C) measured as 0.23 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other AMINOMETHOXY COMPOUNDS

1309. Trimethylamine oxide

[1184-78-7] **C_3H_9NO**



1. *Inorg. Synth.*, 1989, **25**, 107
2. Ringel, C., *Z. Chem.*, 1969, **9**, 188
3. Editor's comments

Energy of decomposition (in range 160—280°C) measured as 1.455 kJ/g.

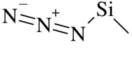
The assessors experienced an explosion while drying the oxide in ethyl ether. Rather drastic precautions are recommended in handling it [1]. A preparation, allowed to stand for a week rather than the day specified, exploded during concentration [2]. Amine oxides from the standard preparation are inclined to retain hydrogen peroxide of 'hydration' unless it is destroyed during work-up. The peroxidate (or diperoxidate) of dimethylamine oxide would be expected to be far more dangerous than the oxide itself [3].

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other N-OXIDES

†1310. Trimethylsilyl azide (Azidotrimethylsilane)

[4648-54-8] **$C_3H_9N_3Si$**



1. Sundermeyer, W., *Chem. Ber.*, 1963, **96**, 1293
2. Thayer, J. S. *et al., Inorg. Chem.*, 1964, **3**, 889
3. West, R. *et al., Chem. Eng. News*, 1984, **62**(24), 4

A standard literature method [1,2] had been used frequently and uneventfully to prepare the azide from trimethylsilyl chloride and sodium azide in presence of aluminium chloride as catalyst. A subsequent duplication led to a violent detonation during distillation of the product, and this was attributed to carry-over of traces of aluminium azides into the distillation flask. Precautions are detailed [3].

Rhenium hexafluoride

1. Fawcett, J. *et al., J. Chem. Soc., Chem. Comm.*, 1982, 958
2. Fawcett, J. *et al., J. Chem. Soc., Dalton Trans.*, 1987, 567—571

Interaction at —60°C in 1,1,2-trichloroethane to give rhenium nitride tetrafluoride is violent and an explosion is possible even with repeated cooling with liquid nitrogen. The final warming to 0°C is also hazardous [1]. If the reactants are mixed at —196°C, at any stage of warming, the reaction can become extremely vigorous and detonate, even with maximum cooling control [2].

Selenium halides

Kennett, F. A. *et al., J. Chem. Soc., Dalton Trans.*, 1982, 851—857

In attempted preparation of poly(selenium nitride), the black solid formed by interaction with selenium tetrabromide in acetonitrile exploded violently within 1 min at 0°C. The solid produced from diselenium tetrachloride in acetonitrile exploded at around 100°C, and in dichloromethane the product exploded in contact with a nickel spatula.

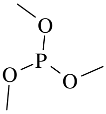
Tungsten hexafluoride

See Azidopentafluorotungsten

See related NON-METAL AZIDES

1311. Trimethyl phosphite

[121-45-9] **$C_3H_9O_3P$**



Magnesium perchlorate

See Magnesium perchlorate: Trimethyl phosphite

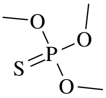
Trimethylplatinum(IV) azide tetramer

See Dodecamethyltetraplatinum(IV)azide: Trimethyl phosphite

See other PHOSPHORUS ESTERS

1312. Trimethyl thiophosphate (Trimethyl phosphorothioate)

[152-18-1] **$C_3H_9O_3PS$**



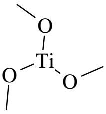
Chlorine

See Chlorine: Trimethyl thionophosphate

See other PHOSPHORUS ESTERS

1313. Titanium(III) methoxide

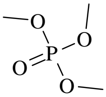
[7245-18-3] **$C_3H_9O_3Ti$**



Bailar, 1973, Vol. 3, 384
A pyrophoric solid.
See other METAL ALKOXIDES

1314. Trimethyl phosphate

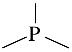
[512-56-1] **$C_3H_9O_4P$**



Anon., *ABCM Quart. Safety Summ.*, 1953, **25**, 3
The residue from a large scale atmospheric pressure distillation of trimethyl phosphate exploded violently. This was attributed to rapid decomposition of the ester, catalysed by the acidic degradation products, with evolution of gaseous hydrocarbons. It is recommended that only small batches of alkyl phosphates should be vacuum distilled and in presence of magnesium oxide to neutralise any acid by-products, and to suppress the acid catalysed reaction.
See other CATALYTIC IMPURITY INCIDENTS, PHOSPHORUS ESTERS

1315. Trimethylphosphine

[594-09-2] **C_3H_9P**

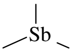


1. Personal experience
2. Labinger, J. A. *et al., Inorg. Synth.*, 1978, **18**, 63

It may ignite in air [1]. It is readily regenerated by heating its air-stable complex with silver iodide [2], which became commercially available in 1983.
See other ALKYLPHOSPHINES

1316. Trimethylantimony (Trimethylstibine)

[594-10-5] **C_3H_9Sb**



Von Schwartz, 1918, 322
It ignites in air.

Halogens

Sidgwick, 1950, 777

Interaction is violent.

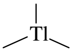
2-Iodoethanol

See 2-Hydroxyethyltrimethylstibonium iodide

See other ALKYLMETALS

1317. Trimethylthallium

[3003-15-4] **C_3H_9Tl**



Sidgwick, 1950, 463

It ignites in air, and is liable to explode violently above 90°C.

Diethyl ether

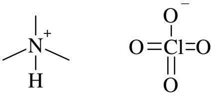
Leleu, *Cahiers*, 1977, (88), 371

The complex with ether explodes at 0°C.

See other ALKYLMETALS

1318. Trimethylammonium perchlorate

[15576-35-9] **$C_3H_{10}ClNO_4$**



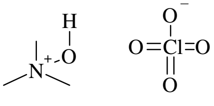
Jain, S. R. *et al., Chem. Abs.*, 1982, **96**, 220110

The salt burns more readily as a propellant than does ammonium perchlorate.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

1319. Trimethylhydroxylammonium perchlorate (Trimethylamine oxide perchlorate)

[22755-36-8] **$C_3H_{10}ClNO_5$**



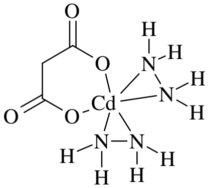
Hofmann, K. A. *et al., Ber.*, 1910, **43**, 2624

The salt, formed from trimethylamine oxide and perchloric acid, explodes on heating, or under a hammer blow.

See other PERCHLORATE SALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

1320. Dihydrazinecadmium(II) malonate (Bis(hydrazine)[propanedioato(2—)] cadmium)

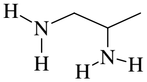
[159793-64-3] **$C_3H_{10}CdN_40_4$**



See HYDRAZINE METAL MALONATES AND SUCCINATES

†1321. 1,2-Diaminopropane (1,2-Propanediamine)

[78-90-0] **$C_3H_{10}N_2$**

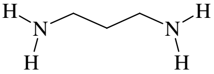


HCS 1980, 798

See other ORGANIC BASES

†1322. 1,3-Diaminopropane (1,3-Propanediamine)

[109-76-2] **$C_3H_{10}N_2$**

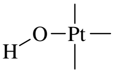


HCS 1980, 361

See other ORGANIC BASES

1323. *S*-Ethylisothiouronium hydrogen sulfate (Ethyl carbamimoniothioate hydrogen sulfate)

[22722-03-8] **$C_3H_{10}N_2O_4S_2$**

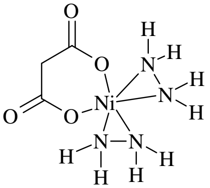


Chlorine

See Chlorine: Nitrogen compounds (reference 4)

1324. Dihydrazinenickel(II) malonate (Bis(hydrazine)[propanedioato(2—)]nickel)

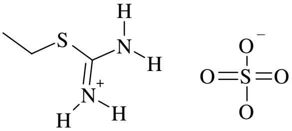
[159793-62-1] **$C_3H_{10}N_4Ni0_4$**



See HYDRAZINE METAL MALONATES AND SUCCINATES

1325. Trimethylplatinum hydroxide

[14477-33-9] **$C_3H_{10}OPt$**



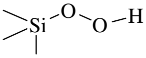
Höchstetter, M. N. *et al., Inorg. Chem.*, 1969, **8**, 400

The compound (originally reported as tetramethylplatinum) and usually obtained in admixture with an alkoxy derivative, detonates on heating.

See other PLATINUM COMPOUNDS

1326. Trimethylsilyl hydroperoxide

[18230-75-6] **$C_3H_{10}O_2Si$**



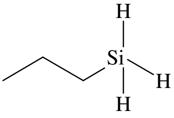
Buncel, E. *et al., J. Chem. Soc.*, 1958, 1551

It decomposes rapidly above 35°C and may have been involved in an explosion during distillation of the corresponding peroxide, which is stable to 135°C.

See related ORGANOMETALLIC PEROXIDES

1327. Propylsilane

[13154-66-0] **$C_3H_{10}Si$**

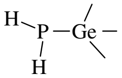


Leleu, *Cahiers*, 1977, (88), 369

It ignites in air.

See other ALKYLSILANES

1328. Trimethylgermylphosphine
[20519-92-0] **$C_3H_{11}GeP$**



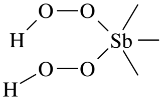
Oxygen

Dahl, A. R. *et al., Inorg. Chem.*, 1975, **14**, 1093

A solution in chloroform at —45°C reacts rapidly with oxygen, and at oxygen pressures above 25 mbar combustion occurs. Dimethyldiphosphinogermane behaves similarly.

See related ALKYLMETALS, PHOSPHINES

1329. Di(hydroperoxy)trimethylantimony(V)
[ ] **$C_3H_{11}O_4Sb$**

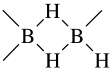


Dodd, M. *et al., Appl. Organomet. Chem.*, 1992, **6**(2), 207

This compound, prepared from trimethylstibine and hydrogen peroxide, exploded violently when heated under vacuum.

See other ORGANOMETALLIC PEROXIDES

1330. Trimethyldiborane
[21107-27-7] **$C_3H_{12}B_2$**

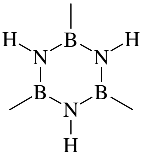


Leleu, *Cahiers*, 1977, (88), 366

It ignites in air.

See other ALKYLBORANES

1331. 2,4,6-Trimethylborazine (*B*-Trimethylborazine)
[5314-85-2] **$C_3H_{12}B_3N_3$**

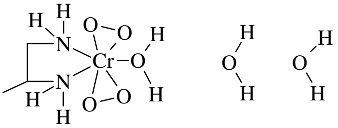


Nitryl chloride

See Nitryl chloride: *B*-Trimethylborazine

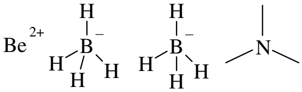
See related BORANES

1332. Aqua-1,2-diaminopropanediperoxochromium(IV) dihydrate
[17185-68-1] **$C_3H_{12}CrN_2O_5.2H_2O$**



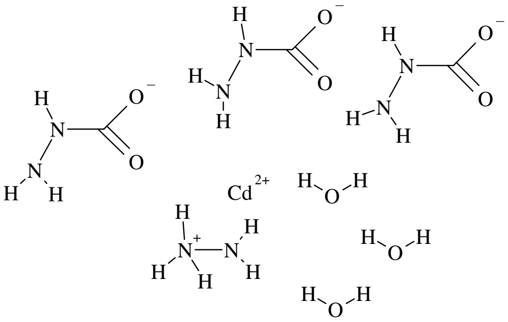
House, D. A. *et al., Inorg. Chem.*, 1966, **5**, 40
Several preparations of the dihydrate exploded spontaneously at 20—25°C, and the aqua complex explodes at 88—90°C during slow heating.
See other AMMINECHROMIUM PEROXOCOMPLEXES

1333. Beryllium tetrahydroborate—trimethylamine
[ ] **$C_3H_{17}B_2BeN$**



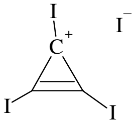
Air, or Water
Burg, A. B. *et al., J. Amer. Chem. Soc.*, 1940, **62**, 3427
The complex ignites in contact with air or water.
See other COMPLEX HYDRIDES

1334. Cadmium hydrazinium tris(hydrazinecarboxylate) trihydrate
[ ] **$C_3H_{20}CdN_8O_9$**



Dhas, N. A. *et al., Chem. Abs.*, 1994, **121**, 314276d
The hydrazinecarboxylate decomposed explosively on heating to 120°C.

1335. Triiodocyclopropenium iodide
[99796-78-8] **C_3I_4**



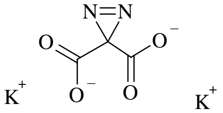
Weiss, R. *et al., Angew. Chem. (Intern. Ed.)*, 1986, **25**, 103

This first example of an ionic halocarbon is extremely explosive, not only when dry, but also upon dissolution in polar solvents (ethanol, acetonitrile). Only 1 mmol of the salt should be prepared in a single experiment, and only samples moist with dichloromethane should be used or handled.

See HALOCARBONS

See other IODINE COMPOUNDS

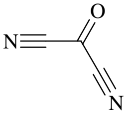
1336. Dipotassium diazirine-3,3-dicarboxylate
[76429-97-5] **$C_3K_2N_2O_4$**



See Diazirine-3,3-dicarboxylic acid

See other DIAZIRINES

1337. Oxopropanedinitrile (Carbonyl dicyanide)
[1115-12-4] **C_3N_2O**



Water

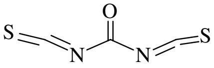
Martin, E. L., *Org. Synth.*, 1971, **51**, 70

The nitrile reacts explosively with water.

See other CYANO COMPOUNDS

See related ACYL HALIDES

1338. Carbonyl diisothiocyanate
[6470-09-3] **$C_3N_2OS_2$**



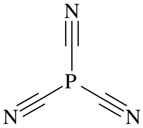
Dimethyl sulfoxide

See Dimethyl sulfoxide: Carbonyl diisothiocyanate

See related CYANO COMPOUNDS

1339. Phosphorus tricyanide

[1116-01-4] **C_3N_3P**



1. Absolom, R. *et al., Chem. & Ind.*, 1967, 1593
2. Smith, T. D. *et al., Chem. & Ind.*, 1967, 1969
3. Mellor, 1971, Vol. 8, Suppl. 3, 583

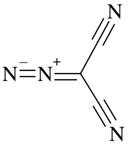
During vacuum sublimation at around 100°C, explosions occurred on 3 occasions. These were attributed to slight leakage of air into the sublimer. The use of joints remote from the heating bath, a high-melting grease, and a cooling liquid other than water (to avoid rapid evolution of hydrogen cyanide in the event of breakage) are recommended, as well as working in a fume cupboard [1]. However, the later publication suggests that the silver cyanide used in the preparation could be the cause of the explosions. On long keeping, it discolours and may then contain the nitride (fulminating silver). Silver cyanide precipitated from slightly acidic solution and stored in a dark bottle is suitable [2]. Phosphorus tricyanide ignites in air if touched with a warm glass rod, and reacts violently with water.

See other CYANO COMPOUNDS

See related NON-METAL HALIDES AND THEIR OXIDES

1340. Diazomalononitrile (Diazodicyanomethane)

[1618-08-2] **C_3N_4**

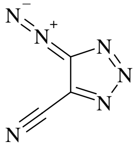


Ciganek, E., *J. Org. Chem.*, 1965, **30**, 4200

Small (mg) quantities melt at 75°C, but larger amounts explode. It also has borderline sensitivity towards static electricity and must be handled with full precautions.

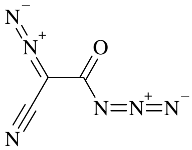
See other CYANO COMPOUNDS, DIAZO COMPOUNDS

1341. 5-Cyano-4-diazo-4*H*-1,2,3-triazole
[16968-06-2] **C_3N_6**



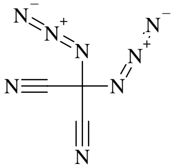
The crystalline solid explodes at the m.p., 125—6°C.
See entry DIAZOAZOLES
See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

1342. Cyanodiazoacetyl azide
[115057-40-4] **C_3N_6O**



Kobolov, M. Yu. *et al., Chem. Abs.*, 1988, **109**, 22908
It explodes on melting.
See other ACYL AZIDES, CYANO COMPOUNDS, DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS

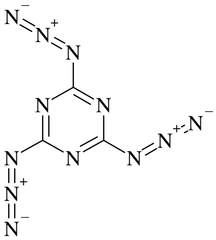
1343. Diazidomalononitrile (Diazidodicyanomethane)
[67880-21-1] **C_3N_8**



MCA Case History No. 820

An ethereal solution of some 100 g of the crude nitrile was allowed to spontaneously evaporate and crystallise. The crystalline slurry so produced exploded violently without warning. Previously such material had been found not to be shock-sensitive to hammer blows, but dry recrystallised material was very shock-sensitive. Traces of free hydrogen azide could have been present, and a metal spatula had been used to stir the slurry, so metal azides could have been formed.
See other CYANO COMPOUNDS, ORGANIC AZIDES

1344. 2,4,6-Triazido-1,3,5-triazine
[5637-83-2] **C_3N_{12}**

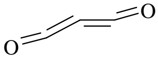


1. Ott, *Ber.*, 1921, **54**, 183
2. Simmonds, R. J. *et al., J. Chem. Soc., Perkin Trans. 1*, 1982, 1824
3. 3. Kessenich, E. *et al., Eur. J. Inorg. Chem.*, 1998, (12), 2013

This polyazide (82.3% N) explodes on impact, shock or rapid heating to 170—180°C [1]. X-ray crystallographers report that explosivity increases with purity and crystal size [3]. When preparing 2,4-diazido-6-dimethylamino-1,3,5-triazine from the 2,4-dichloro compound and sodium azide, there is the possibility of forming the triazido derivative, which detonates violently when touched. Reactions involving organic chlorides and excess sodium azide are extremely dangerous [2].

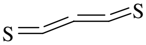
See other HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

†1345. Propadiene-1,3-dione ('Carbon suboxide')
[504-64-3] **C_3O_2**



See related ACID ANHYDRIDES

1346. Propadienedithione (Carbon subsulfide)
[627-34-9] **C_3S_2**

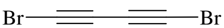


Mellor, 1940, Vol. 6, 88

A red oil decomposing to a black polymer, explosively if heated rapidly to 100-120°C. Probably highly endothermic.

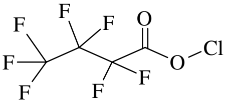
See other ENDOTHERMIC COMPOUNDS, NON-METAL SULFIDES

1347. 1,4-Dibromo-1,3-butadiyne
[36333-41-2] **C_4Br_2**



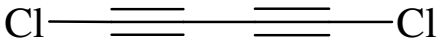
Petterson, R. C. *et al., Chem. Eng. News*, 1977, **55**(48), 36
An explosion temperature has been published, but a solvent-free sample standing unheated under nitrogen exploded after 1 h.
See other HALOACETYLENE DERIVATIVES

1348. Heptafluorobutyryl hypochlorite
[71359-62-1] **$C_4ClF_7O_2$**



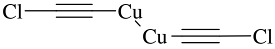
Tari, I. *et al., Inorg. Chem.*, 1979, **18**, 3205—3208
It is thermally unstable above 22°C and explosive in the gas phase at pressures above 27—62 mbar.
See entry ACYL HYPOHALITES (reference 1)

1349. 1,4-Dichloro-1,3-butadiyne
[51104-87-1] **C_4Cl_2**



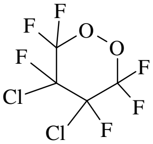
Sorbe, 1968, 50
It explodes above 70°C.
See other HALOACETYLENE DERIVATIVES

1350. Copper(I) chloroacetylide
[ ] **$C_4Cl_2Cu_2$**



Kirk-Othmer, 1964, Vol. 5, 204
Explosive.
See other HALOACETYLENE DERIVATIVES, HEAVY METAL DERIVATIVES

1351. 4,5-Dichloro-3,3,4,5,6,6-hexafluoro-1,2-dioxane
[ ] **$C_4Cl_2F_6O_2$**



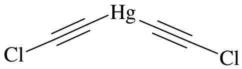
Haszeldine, R. N. *et al., J. Chem. Soc.*, 1959, 1089

Formed in the controlled oxidation of chlorotrifluoroethylene, it explodes violently on heating.

See other CYCLIC PEROXIDES

1352. Mercury bis(chloroacetylide)

[64771-59-1] **C_4Cl_2Hg**



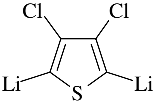
Whitmore, 1921, 119

It explodes fairly violently above the m.p., 185°C.

See other HALOACETYLENE DERIVATIVES, MERCURY COMPOUNDS, METAL ACETYLIDES

1353. 3,4-Dichloro-2,5-dilithiothiophene

[29202-04-8] **$C_4Cl_2Li_2S$**



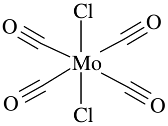
Gilman, H., private comm., 1971

The dry solid is explosive, though relatively insensitive to shock.

See other ORGANOLITHIUM REAGENTS

1354. Tetracarbonylmolybdenum dichloride

[15712-13-7] **$C_4Cl_2MoO_4$**



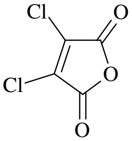
Newton, W. E. *et al., Inorg. Synth.*, 1978, **18**, 54

If stored at ambient temperature, the complex decomposes to a dark pyrophoric powder.

See related CARBONYLMETALS

1355. Dichloromaleic anhydride

[1122-17-4] **$C_4Cl_2O_3$**



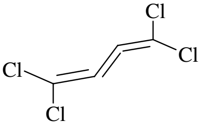
Sodium chloride, Urea

Bott, D. C., private comm., 1980

To prepare dichloromaleimide, the 3 components are melted together with stirring. At 118°C the vigorous exothermic reaction sets in, and rapid ice cooling must then be applied to prevent explosion.

See other ACID ANHYDRIDES

1356. 1,1,4,4-Tetrachlorobutatriene
[19792-18-8] **C_4Cl_4**



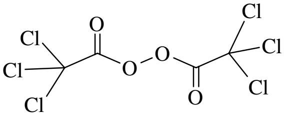
Heinrich, B. *et al., Angew. Chem. (Intern. Ed.)*, 1968, **7**, 375

One of the by-products formed by heating this compound is an explosive polymer.

See other HALOALKENES

See related DIENES

1357a. Bis(trichloroacetyl) peroxide
[2629-78-9] **$C_4Cl_6O_4$**

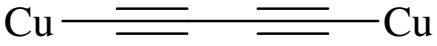


1. Swern, 1971, Vol. 2, 815
2. Miller, W. T., *Chem. Abs.*, 1952, **46**, 7889e

Pure material explodes on standing at ambient temperature [1], but the very shock-sensitive solid may be stored safely in trichlorofluoromethane solution at —20°C [2].

See other DIACYL PEROXIDES

1357b. Dicopper Butadiynide (Dicopper Diacetylide)
[30645-11-5] **C_4Cu_2**



Cataldo, F., *Eur. J. Solid State Inorg. Chem.*, 1998, **35**(3), 81

It was shown that, on aging in air, copper(I) acetylide oxidises to this, which was also prepared independently from butadiyne. It also seems to result from reaction of copper solutions of mixed I and II valencies with acetylene. Further oxidation appears to give higher homologues. The explosive properties remain. Essentially, this is the Cu II mediated oxidative coupling, by which higher acetylenes are normally prepared synthetically, operating spontaneously.

See other METAL ACETYLIDES

1358. Tetracarbon monofluoride

[12774-81-1] **C_4F**

C_4F

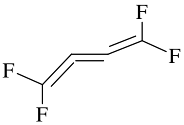
Bailar, 1973, Vol. 1, 1271

Though generally inert, rapid heating causes deflagration.

See related HALOALKANES, NON-METAL HALIDES

1359. 1,1,4,4-Tetrafluorobutatriene

[2252-95-1] **C_4F_4**



Martin, E. L. *et al., J. Amer. Chem. Soc.*, 1959, **81**, 5256

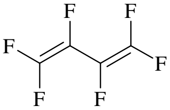
In the liquid state, it explodes above —5°C.

See other HALOALKENES

See related DIENES

1360. Perfluorobutadiene

[87-68-3] **C_4F_6**



Feast, W. J., personal communication, 1993.

Attempts to use this material as a monomer are not recommended as reaction is uncontrollable and it is liable to explode.

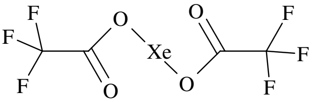
Bromine perchlorate

See Bromine perchlorate: Perfluorobutadiene

See other DIENES, HALOALKENES

1361. Bis(trifluoroacetoxy)xenon

[21961-22-8] **$C_4F_6O_4Xe$**



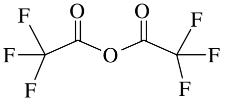
Kirk Othmer, 1980, Vol 12, 293

Detonates easily and should be handled with extreme care.

See other XENON COMPOUNDS

1362. Trifluoroacetic anhydride

[407-25-0] **$C_4F_6O_3$**



Dimethyl sulfoxide

See Dimethyl sulfoxide: Trifluoroacetic anhydride

Nitric acid, 1,3,5-Triacetylhexahydro-1,3,5-triazine

See Nitric acid: 1,3,5-Triacetylhexahydrotriazine

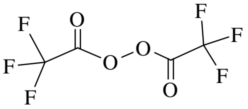
Nitric acid, 1,3,5-Triazine

See Nitric acid: 1,3,5-Triazine, etc.

See other ACID ANHYDRIDES

1363. Bis(trifluoroacetyl) peroxide

[383-73-3] **$C_4F_6O_4$**



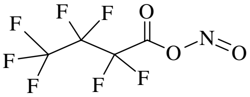
Swern, 1971, Vol. 2, 815

Pure material explodes on standing at ambient temperature.

See other DIACYL PEROXIDES

1364. Heptafluorobutyryl nitrite

[663-25-2] **$C_4F_7NO_3$**



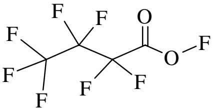
Banks, R. E. *et al., J. Chem. Soc. (C)*, 1966, 1351

This may be explosive like its lower homologues, and suitable precautions are neccessary during heating or distillation.

See other ACYL NITRITES

1365. Heptafluorobutyryl hypofluorite

[ ] **$C_4F_8O_2$**



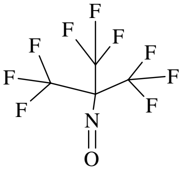
Cady, G. H. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 2020

The vapour slowly decomposes at ambient temperature, but will decompose explosively on spark initiation.

See other ACYL HYPOHALITES

1366. Perfluoro-*tert*-nitrosobutane (Tris(trifluoromethyl)nitrosomethane)

[354-93-8] **C_4F_9NO**



Nitrogen oxides

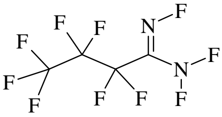
Sterlin, S. R. *et al.*, Russ. Pat. 482 432, 1975

The danger of explosions during oxidation of the nitroso compound to perfluoro-*tert*-butanol with nitrogen oxides and subsequent hydrolysis, was reduced by working in a flow system at 160—210°C with 8—10% of nitrogen oxides in air, and using conc. sulfuric acid for hydrolysis.

See other NITROSO COMPOUNDS

1367. Decafluorobutyramidine

[41409-50-1] **$C_4F_{10}N_2$**



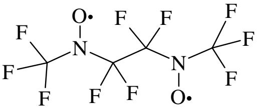
Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3096—3097

A shock-sensitive explosive

See other *N,N,N'*-TRIFLUOROAMIDINES

1368. Decafluoro-2,5-diazahexane 2,5-dioxyl

[36525-64-1] **$C_4F_{10}N_2O_2$**



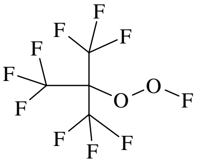
Preparative hazard

Banks, R. E. *et al., J. Chem. Soc., Perkin Trans. 1*, 1974, 2535—2536

During an increased-scale preparation of the dioxyl by permanganate oxidation of the hydrolysate of a nitrosotrifluoromethane—tetrafluoroethylene—phosphorus trichloride adduct, an impurity in the dioxyl, trapped out at —96°C (?—196°C) and < 2.5 mbar, caused a violent explosion to occur when the trap content was allowed to warm up. A procedure to eliminate the hazard is detailed.

See related N-OXIDES

1369. Perfluoro-*tert*-butyl peroxyhypofluorite
[66793-67-7] **$C_4F_{10}O_2$**



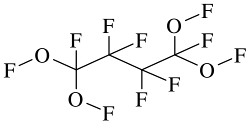
Yu, S.-L. *et al., Inorg. Chem.*, 1978, **17**, 2485

It explodes when warmed to 22°C in a sealed tube with a liquid phase present, but is apparently stable in the gas phase alone.

See other ORGANIC PEROXIDES

See related HYPOHALITES

1370. 1,1,4,4-Tetrakis(fluoroxy)hexafluorobutane
[22410-18-0] **$C_4F_{10}O_4$**

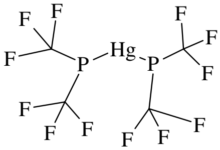


Sekiya, A. *et al., Inorg. Chem.*, 1980, **19**, 1329

It explodes energetically at —20°C.

See other BIS(FLUOROOXY)PERHALOALKANES

1371. Di[bis(trifluoromethyl)phosphido]mercury
[ ] **$C_4F_{12}HgP_2$**



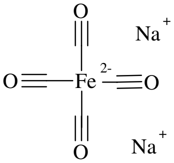
Grobe, J. *et al., Angew. Chem. (Intern. Ed.)*, 1972, **11**, 1098

It ignites in air.

See other MERCURY COMPOUNDS

See related ALKYLPHOSPHINES

1372. Sodium tetracarbonylferrate(2—)
[14878-31-0] $C_4FeNa_2O_4$

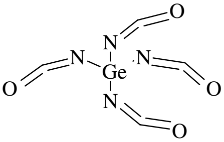


1. Collman, J. P., *Accts. Chem. Res.*, 1975, **8**, 343
2. Finke, R. G. *et al., Org. Synth.*, 1979, **59**, 102—112

It is extremely oxygen-sensitive and ignites in air [1]. The salt solvated with 1.5 mols of dioxane is similarly reactive [2].

See related CARBONYLMETALS

1373. Germanium isocyanate (Tetraisocyanatogermane)
[4756-66-5] $C_4GeN_4O_4$



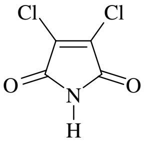
Water

Johnson, D. H., *Chem. Rev.*, 1951, **48**, 287

The rate of exothermic hydrolysis becomes dangerously fast above 80°C.

See related CYANO COMPOUNDS, METAL CYANATES

1374. Dichloromaleimide (3,4-Dichloro-2,5-pyrrolidinedione)
[1193-54-0] $C_4HCl_2NO_2$

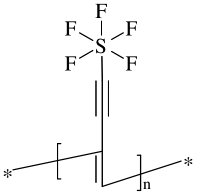


Preparative hazard

See Dichloromaleic anhydride: Sodium chloride, Urea

1375. Poly(1-pentafluorothio-1,2-butadiyne)

[84864-30-2] **$(C_4HF_5S)_n$**



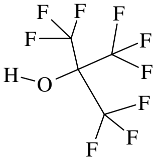
Kovacina, T. A. *et al., Ind. Eng. Chem., Prod. Res. Dev.*, 1983, **22**, 170—172

The insoluble polymer formed in the liquid phase was pressure- and shock-sensitive and should not be heated above 25°C. Cutting with a razor or breaking the polymer causes detonation and ignition.

See related DIENES, HALOALKENES

1376. Perfluoro-*tert*-butanol

[2378-02-1] **C_4HF_9O**

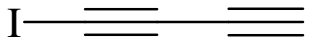


Preparative hazard

See Perfluoro-*tert*-nitrosobutane: Nitrogen oxides

1377. 1-Iodo-1,3-butadiyne

[6088-91-1] **C_4HI**



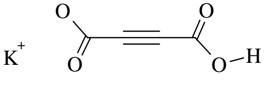
1. Schluhbach, H. H. *et al., Ann.*, 1951, **573**, 118, 120
2. Kloster-Jensen, E., *Tetrahedron*, 1966, **22**, 969

Crude material exploded violently at 35°C during attempted vacuum distillation, and temperatures below 30°C are essential for safe handling [1]. A sample of pure material exploded on scratching under illumination [2].

See other HALOACETYLENE DERIVATIVES, IRRADIATION DECOMPOSITION INCIDENTS

1378. Potassium hydrogen acetylenedicarboxylate (Butynedioic acid monopotassium salt)

[928-04-1] **C_4HKO_4**



Energy of decomposition (in range 170—360°C) measured as 0.775 kJ/g by DSC, and T_{ait24} was determined as 202°C by adiabatic Dewar tests, with an apparent energy of activation of 155 kJ/mol.

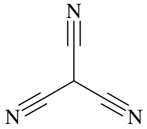
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other ACETYLENIC COMPOUNDS

See related ORGANIC ACIDS

1379. Cyanoform (Tricyanomethane)

[454-50-2] **C_4HN_3**



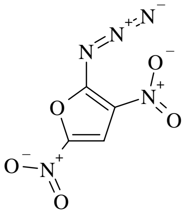
1. Stull, 1977, 19
2. Rodd, 1976, **IE**, 333

As expected for a tricyano compound, it is highly endothermic (ΔH_f° (s) +348.1 kJ/mol, 3.78 kJ/g), so its stability seems dubious [1]. However, because of isomerisation to the acidic dicyano-enimine $(NC)_2C{=}C{=}NH$, it is considerably stabilised and the silver and sodium salts surprisingly are described as stable [2].

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

1380. 2-Azido-3,5-dinitrofuran

[70664-49-2] **$C_4HN_5O_5$**



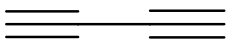
Sitzmann, M. E., *J. Heterocycl. Chem.*, 1979, **16**, 477—480

Very sensitive to heat and impact.

See other ORGANIC AZIDES, POLYNITROARYL COMPOUNDS

†1381. 1,3-Butadiyne

[460-12-8] **C_4H_2**



1. Armitage, J. B. *et al., J. Chem. Soc.*, 1951, 44
2. Mushii, R. Y. *et al., Khim. Prom.*, 1963, **39**, 109
3. Moshkovich, F. B. *et al., Khim. Prom.*, 1965, **41**, 137—139
4. Anon., *Chem. Age*, 1951, **64**(1667), 955—958
5. Schilling, H. *et al.*, Ger. Pat. 860 212, 1956

Potentially very explosive, it may be handled and transferred by low temperature distillation. It should be stored at —25°C to prevent decomposition and formation of explosive polymers [1]. The critical pressure for explosion is 0.04 bar, but presence of 15—40% of diluents (acetylene, ammonia, carbon dioxide or nitrogen) will raise the critical pressure to 0.92 bar [2]. Further data on attenuation by inert diluents of the explosive decomposition of the diyne are available [3]. During investigation of the cause of a violent explosion in a plant for separation of higher acetylenes, the most important finding was to keep the concentration of 1,3-butadiyne below 12% in its mixtures. Methanol is a practical diluent [4]. The use of butane (at 70 mol%) or other diluents to prevent explosion of 1,3-butadiyne when heated under pressure has been claimed [5]. It polymerises rapidly above 0°C.

Arsenic pentafluoride

Russo, P. J. *et al., J. Chem. Soc., Chem. Comm.*, 1982, 53—54

Polymerisation of the diyne by arsenic pentafluoride at low temperature may be explosive if too rapid mixing in the gas phase, or too rapid warming of the solids from —196°C, is permitted for 200 mg quantities.

See other POLYMERISATION INCIDENTS

Silver nitrate

Grignard, 1935, Vol. 3, 181

Reaction with ammoniacal silver nitrate gives a very explosive friction-sensitive silver salt.

See METAL ACETYLIDES

See other ALKYNES, PEROXIDISABLE COMPOUNDS

1382. Poly(butadiyne)

[61565-16-0] **$(C_4H_2)_n$**

$(\text{-CH=CHC}\equiv\text{C-})_n$

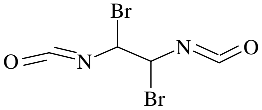
Preparative hazard

See 1,3-Butadiyne: Arsenic pentafluoride

See related ALKYNES

1383. 1,2-Dibromo-1,2-diisocyanatoethane polymers

[51877-12-4] **$(C_4H_2Br_2N_2O_2)_{2 \text{ or } 3}$**



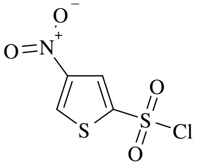
2-Phenyl-2-propyl hydroperoxide

See 2-Phenyl-2-propyl hydroperoxide: 1,2-Dibromo-1,2-diisocyanatoethane polymers

See related CYANO COMPOUNDS, ORGANIC ISOCYANATES

1384. 4-Nitrothiophene-2-sulfonyl chloride

[40358-04-1] **$C_4H_2ClNO_4S_2$**



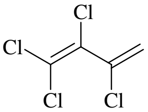
Libman, D. D., *private comm.*, 1968

After distilling the chloride up to 147°C/6 mbar, the residue decomposed vigorously.

See other NITROACYL HALIDES

1385. 1,1,2,3-Tetrachloro-1,3-butadiene

[1637-31-6] **$C_4H_2Cl_4$**



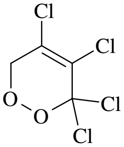
It autoxidises to an unstable peroxide.

See 3,3,4,5-Tetrachloro-3,6-dihydro-1,2-dioxin

See other DIENES, HALOALKENES, PEROXIDISABLE COMPOUNDS

1386. 3,3,4,5-Tetrachloro-3,6-dihydro-1,2-dioxin

[ ] **$C_4H_2Cl_4O_2$**



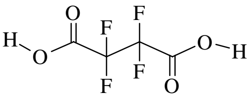
Akopyan, A. N. *et al., Chem. Abs.*, 1975, **82**, 111537

This autoxidation product of 1,1,2,3-tetrachloro-1,3-butadiene exploded during attempted vacuum distillation.

See other CYCLIC PEROXIDES

1387. Perfluorosuccinic acid (Tetrafluorobutanedioic acid)

[377-38-8] **$C_4H_2F_4O_2$**



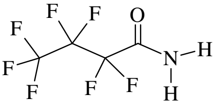
Caesium fluoride, Fluorine

See Fluorine: Caesium fluoride, etc.

See other ORGANIC ACIDS

1388. Heptafluorobutyramide

[662-50-0] **$C_4H_2F_7NO$**

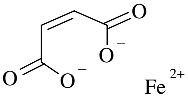


Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Fluoroamides

1389. Iron(II) maleate

[7705-12-6] **$C_4H_2FeO_4$**



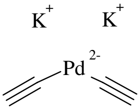
Schwab, R. F. *et al., Chem. Eng. Prog.*, 1970, **66**(9), 53

The finely divided maleate, a by-product of phthalic anhydride manufacture, is subject to rapid aerial oxidation above 150°C, and has been involved in plant fires.

See other HEAVY METAL DERIVATIVES, PYROPHORIC MATERIALS

1390. Potassium diethynylpalladate(2—)

[ ] **$C_4H_2K_2Pd$**



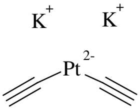
Air, or Water

Immediately pyrophoric in air, explosive decomposition with aqueous reagents; the sodium salt is similar.

See entry COMPLEX ACETYLIDES

1391. Potassium diethynylplatinate(2—)

[ ] **$C_4H_2K_2Pt$**



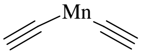
Air, or Water

Pyrophoric in air, explosive decomposition with water; the sodium salt is similar.

See entry COMPLEX ACETYLIDES

1392. Manganese(II) bis(acetylide)

[ ] **C_4H_2Mn**



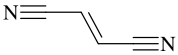
Bailar, 1973, Vol. 3, 855

A highly explosive compound.

See other METAL ACETYLIDES

1393. Fumarodinitrile

[764-42-1] **$C_4H_2N_2$**



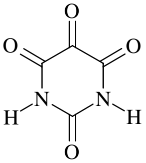
Highly endothermic: ΔH_f° 268 kJ/mole, 3.4 kJ/g. Energy of decomposition (in range 340—380°C) measured as 0.454 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

1394. Pyrimidine-2,4,5,6-(1*H*,3*H*)-tetrone (‘Alloxan’)

[50-71-5] **$C_4H_2N_2O_4$**



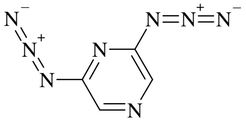
1. Wheeler, A. S., and Bogert, M. T., *J. Amer. Chem,. Soc.*, 1910, **32**, 809
2. Gartner, R. A., *J. Amer. Chem. Soc.*, 1911, **33**, 85
3. Franklin, E. C., *J. Amer. Chem. Soc.*, 1901, **23**, 1362
4. Sorbe, 1968, 140

The tetrone slowly decomposes during storage at ambient temperature with generation of carbon dioxide. Two separate pairs of incidents involving bursting of bottles [1], and of pressure generation [2,3], were reported. It also explodes at temperatures above 170°C [4].

See Imidazoline-2,4-dithione

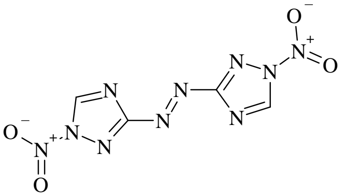
See other GAS EVOLUTION INCIDENTS

1396. 2,6-Diazidopyrazine
[74273-75-9] **$C_4H_2N_8$**



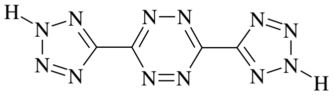
Shaw, J. T. *et al., J. Heterocycl. Chem.*, 1980, **17**, 14
It is heat- and impact-sensitive, exploding at 200°C, or under a hammer-blow.
See other HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1397a. 3,3′-Azo-(1-nitro-1,2,4-triazole)
[104364-15-0] **$C_4H_2N_{10}O_4$**



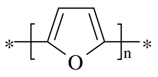
Lee, K. Y., *Energy Res. Abstr.*, 1985, **10**(17), 34672
A candidate for high-energy propellant applications.
See other AZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, N—NITRO COMPOUNDS, TRIAZOLES

1397b. 3,6-Bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine
[68594-20-7] **$C_4H_2N_{12}$**



Sauer, J. *et al., Eur. J. Org. Chem.*, 2001, (4), 697
This species, advanced as a useful synthetic reagent, should not be dried in above 200 mg quantities. Nor should dry material be heated, scratched or exposed to electrostatic charge. The 1,4-dihydro-compound is also explosive, but can be stored in a refrigerator.
HIGH-NITROGEN COMPOUNDS

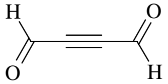
1398. Poly(furan-2,5-diyl)
[51325-04-3] **$(C_4H_2O)_n$**



Perchlorate ions

See entry PERCHLORATE-DOPED CONDUCTING POLYMERS

1399. Acetylenedicarboxaldehyde (1,4-Dioxobut-2-yne) [21251-20-7] $C_4H_2O_2$

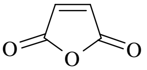


Gorgues, A. *et al., Tetrahedron*, 1990, **46**(8), 2817

The solid explodes, flamelessly, even under nitrogen, at its melting point, —11°C. The vapour was handled at reduced pressure up to 60°C.

See other ACETYLENIC COMPOUNDS, ALDEHYDES

1400. Maleic anhydride (2,5-Dihydrofuran-2,5-dione) [108-31-6] $C_4H_2O_3$



(*MCA SD-88*, 1962); *HCS 1980*, 605; *RSC Lab. Hazards Data Sheet No. 53*, 1983

1. Vaughn, C. B. *et al., J. Loss Prevention*, 1993, **6**(1), 61
2. Grotenfendt, R. H. *et al., J. Haz. Mat.*, 2004, **115**(1-3), 115

Energy of decomposition (in range 260—370°C) measured as 0.92 kJ/g.A fire within a maleic acid plant left pipework glowing red hot. Investigation of possible sources of ignition showed that the anhydride, spread on insulation materials, undergoes runaway autoxidation/decomposition from 190°C [1]. A maleic hydride tank ruptured after a complicated series of events, starting with a plug in a recirculating line, the content of which was then overheated to decomposition, and blew the plug into the tank, damaging an interior heating/cooling line, which allowed water to seep into the tank giving slow hydrolytic heating until thermal decomposition ruptured the whole [2]

See also INSULATION, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Bases, or Cations

1. Vogler, C. E. *et al., J. Chem. Eng. Data*, 1963, **8**, 620
2. Davie, W. R., *Chem. Eng. News.*, 1964, **42**(8), 41
3. *MCA Case History No. 622*
4. *MCA Case History No. 2032*

Maleic anhydride decomposes exothermically, evolving carbon dioxide, in the presence of alkali- or alkaline earth- metal or ammonium ions, dimethylamine, triethylamine, pyridine or quinoline, at temperatures above 150°C [1]. Sodium ions and pyridine are particularly effective, even at concentrations below 0.1%, and decomposition is rapid [2]. An industrial incident involved gas-rupture of a large insulated tank of semi-solid maleic anhydride which had been contaminated with sodium hydroxide. Use of additives to reduce the sensitivity of the anhydride has been described [3]. Accidental transfer of an aqueous solution of sodium 2-benzothiazolethiolate into a bulk storage tank of the anhydride led to eventual explosive destruction of the tank [4].

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

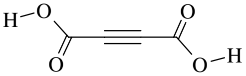
1-Methylsilacyclopenta-2,4-diene

See 1-Methylsilacyclopenta-2,4-diene: Dienophiles

See other ACID ANHYDRIDES

1401. Acetylenedicarboxylic acid

[142-45-0] **$C_4H_2O_4$**



Energy of decomposition (in range 140—270°C) measured as 1.355 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Copper salts

Zamudio, W. *et al., Bol. Soc. Chil. Quim.*, 1994, **39**(4), 339

Aqueous solutions of copper acetylenedicarboxylates decompose thermally to precipitate explosive copper acetylides. Presumably other elements readily forming explosive acetylides might do likewise.

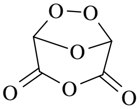
See Copper(II) acetylide

See also METAL ACETYLIDES

See other ACETYLENIC COMPOUNDS, ORGANIC ACIDS

1402. Maleic anhydride ozonide

[101672-17-7] **$C_4H_2O_6$**



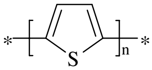
Briner, E. *et al., Helv. Chim. Acta*, 1937, **20**, 1211

It explodes on warming to —40°C.

See other OZONIDES

1403. Poly(thiophene)

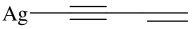
[25233-34-5] **$(C_4H_2S)_n$**



Perchlorate ions

See entry PERCHLORATE-DOPED CONDUCTING POLYMERS

1404. Silver buten-3-ynide
[15383-68-3] **C_4H_3Ag**



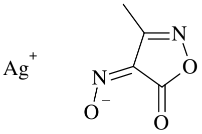
Alone, or Ammonia, or Nitric acid

1. Willstätter, R. *et al., Ber.*, 1913, **46**, 535—538
2. Grignard, 1935, Vol. 3, 187

The silver salt, which deflagrates on heating, explodes if moistened with fuming nitric acid [1], or with ammonia solution [2].

See other METAL ACETYLIDES, SILVER COMPOUNDS

1405a. Silver 3-methylisoxazolin-4,5-dione-4-oximate
[70247-51-7] **$C_4H_3AgN_2O_3$**



Wentrup, C. *et al., Angew. Chem. (Intern. Ed.)*, 1979, **18**, 467

It explodes on rapid heating. On slow heating under vacuum, it gives dangerously explosive silver fulminate.

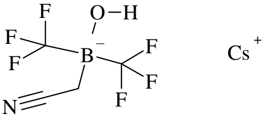
See Fulminic acid (reference 2)

See also Sodium 3-methylisoxazolin-4,5-dione-4-oximate

See other N—O COMPOUNDS, SILVER COMPOUNDS

See related OXIMES

1405b. Caesium cyanomethylbis(trifluoromethyl)hydroxyborate (Cesium cyanomethylhydroxybis(trifluoromethyl)borate(1-))
[251962-61-5] **$C_4H_3BCsF_3NO$**



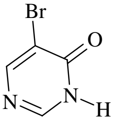
Brauer, D. J. *et al., J. Fluor. Chem.*, 1999, **98**(2), 143

This salt explodes spontaneously as the crystalline solid, although stable in solution. The potassium analogue explodes on heating to 170°C.

See also CYANO COMPOUNDS

See related METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

1406. 5-Bromo-4-pyrimidinone
[19808-30-1] **$C_4H_3BrN_2O$**



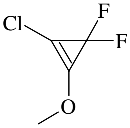
Preparative hazard

Dietsche, T. J. *et al., Chem. Eng. News*, 1995, **78**(28), 4

A literature procedure whereby bromopyrimidine is oxidised by excess peroxyacetic acid in acetone, with sulfuric acid catalysis, was being scaled up. The crude product from the fourth batch at two molar scale was filtered out and allowed to dry to dry in the sintered glass funnel over the weekend. An explosion occurred when it was scraped out to complete purification on the Monday. This was considered due to acetone peroxides, which had probably concentrated locally by wicking or sublimation.

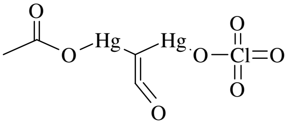
See CYCLIC PEROXIDES, SINTERED GLASS

1407. 1-Chloro-3,3-difluoro-2-methoxycyclopropene
[59034-34-3] **$C_4H_3ClF_2O$**



See entry FLUORINATED CYCLOPROPENYL METHYL ETHERS

1408. Acetoxymercurio(perchloratomercurio)ethenone
[73399-68-5] **$C_4H_3ClHg_2O_7$**



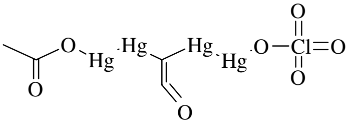
Blues, E. T. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 1043

It is dangerously explosive.

See other MERCURY COMPOUNDS

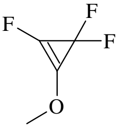
See related METAL PERCHLORATES

1409. Acetoxydimercurio(perchloratodimercurio)ethenone
[73399-71-0] **$C_4H_3ClHg_4O_7$**



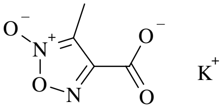
Blues, E.T. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 1043
It is dangerously explosive.
See other MERCURY COMPOUNDS
See related METAL PERCHLORATES

1410. 1,3,3-Trifluoro-2-methoxycyclopropene
[59034-32-1] **$C_4H_3F_3O$**



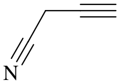
See entry FLUORINATED CYCLOPROPENYL METHYL ETHERS

1411. Potassium 3-methylfurazan-4-carboxylate 2-oxide
[37895-51-5] **$C_4H_3KN_2O_4$**



Gasco, A. *et al., Tetrahedron Lett.*, 1974, 630 (footnote 2)
The dried salt explodes violently on heating, impact or friction.
See other FURAZAN *N*-OXIDES

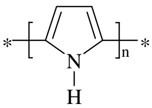
1412. 3-Cyanopropyne (1-Butyne-4-nitrile)
[2235-08-7] **C_4H_3N**



Reddy, G. S. *et al., J. Amer. Chem. Soc.*, 1961, **83**, 4729
After preparation from interaction of 3-bromopropyne with copper(I) cyanide and filtration from copper salts, an explosion occurred during distillation of the evaporated filtrate at 45—60°C/66 mbar. This was attributed to explosion of some dissolved copper acetylide(s). After refiltration the product was again distilled at 45—48°C/53

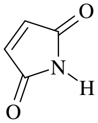
mbar without incident, and it appeared to be stable, unlike true haloalkynes. However it is undoubtedly an endothemic compound with its two triple bonds.
See other ACETYLENIC COMPOUNDS, CYANO COMPOUNDS
See related HALOACETYLENE DERIVATIVES

1413. Poly(pyrrole)
[30604-81-0] **$(C_4H_3N)_n$**



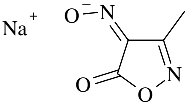
Perchlorate ions
See entry PERCHLORATE-DOPED CONDUCTING POLYMERS

1414. Maleimide
[541-59-3] **C_4H_3NO**



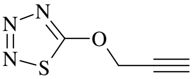
Energy of decomposition (in range 140—300°C) measured as 0.49 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

1415. Sodium 3-methylisoxazolin-4,5-dione-4-oximate
[70247-50-6] **$C_4H_3N_2NaO_3$**



Wentrup, C. *et al., Angew. Chem. (Intern. Ed.)*, 1979, **18**, 467
It explodes on rapid heating, like the analogous silver salt and 3-phenyl derivative.
See other N—O COMPOUNDS
See related OXIMES

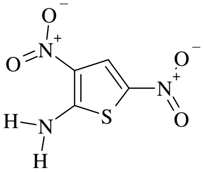
1416. 5-(Prop-2-ynyloxy)-1,2,3,4-thiatriazole
[ ] **$C_4H_3N_3OS$**



Banert, K. *et al., Angew. Chem. (Int.)*, 1992, **31**(7), 866

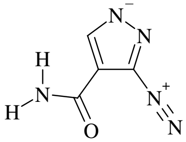
Decomposes in solution at 0°C but can be handled, with caution even sublimed, as an explosive crystalline solid, m.p. 66°C.
See other ACETYLENIC COMPOUNDS, N—S COMPOUNDS, THIATRIAZOLES

1417. 2-Amino-3,5-dinitrothiophene
[2045-70-7] **$C_4H_3N_3O_4S$**



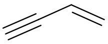
Fast flame propagation occurs on heating the powder moderately.
See entry HIGH RATE DECOMPOSITION

1418. 3-Diazoniopyrazolide-4-carboxamide
[102613-59-2] **$C_4H_3N_5O$**



Cheng, C. C. *et al., J. Med. Chem.*, 1986, **29**, 1546
Though the preparative method is suitable for large scale synthesis, the product must be handled with care. On rapid heating, the internal diazonium salt decomposes violently at 155—160°C accompanied by a sharp sound. The dried powder should not be scratched with a metal spatula or ground finely.
See other DIAZONIUM SALTS, HIGH-NITROGEN COMPOUNDS

†1419. Buten-3-yne (Vinylacetylene)
[689-97-4] **C_4H_4**



1. Hennion, G. F. *et al., Org. Synth.*, 1963, Coll. Vol. 4, 684
2. Rutledge, 1968, 28
3. Strizhevskii, I. I. *et al., Chem. Abs.*, 1973, **78**, 98670
4. Vervalin, 1973, 38—43

It must be stored out of contact with air to avoid the formation of explosive (peroxidic) compounds [1]. The sodium salt is a safe source of butenyne for synthetic use [2]. Explosive properties of the liquid and gaseous hydrocarbon alone, or diluted with decahydronaphthalene, were determined [3]. Mechanical failure of a compressor circulating the gaseous hydrocarbon through a reaction system led to local overheating and explosive decomposition, which propagated throughout the large plant [4]. As anticipated for a multiply unsaturated hydrocarbon, vinylacetylene is strongly endothermic (ΔH_f° (g) +143.5 kJ/mol, 2.76 kJ/g).

See other ENDOTHERMIC COMPOUNDS

1,3-Butadiene

1. Jarvis, H. C., *Chem. Eng. Progr.*, 1971, **67**(6), 41—44
2. Freeman, R. H. *et al., Chem. Eng. Progr.*, 1971, **67**(6), 45—51
3. Keister, R. G. *et al., Loss Prev.*, 1971, **5**, 67—75
4. Carver, F. W. S. *et al., Proc. 5th Symp. Chem. Proc. Haz.*, No. 39a, 99—116, London, IChE, 1975

Unusual conditions in the main fractionation column separating product butadiene from by-product butenyne (vinylacetylene, thought to be safe at below 50 mol% concentration) caused the concentration of the latter to approach 60% in part of the column as fractionation proceeded. Explosive decomposition, possibly initiated by an overheated unstable organic material derived from sodium nitrite, destroyed the column and adjacent plant [1,2]. Subsequent investigation showed that all mixtures of butenyne and butadiene can reproducibly be caused to react exothermically and then decompose explosively at appropriately high heating rates under pressure. Butadiene alone will behave similarly at higher heating rates and pressures [3]. Another study of the detailed mechanism and type of decomposition of C_4 hydrocarbons containing butenyne showed that both were dependent on energy of initiation and time of application, as well as on the composition and phases present [4].

See Sodium nitrite: 1,3-Butadiene

Oxygen

1. Dolgopolskii, I. M. *et al., Chem., Abs.*, 1958, **52**, 19904g
2. Gosa, V. *et al., Rev. Chim.* (Bucharest), 1981, **32**, 1103—1105
3. Ionescu, N. I. *et al., Rev. Chim.* (Bucharest), 1982, **33**, 1021—1026

The rate of absorption of oxygen by liquid butenyne increased with time, and eventually a yellow liquid phase separated. After evaporation of excess hydrocarbon, the yellow peroxidic liquid was explosive. Presence of 5% of chloroprene increased the rate of absorption 5—6-fold, and of 2% of water decreased the rate by 50%, but residues were explosive in each case [1]. Explosive combustion in admixture with oxygen has been studied [2], and the effects of presence of nitrogen upon explosion parameters were determined [3].

Silver nitrate

Grignard, 1935, Vol. 3, 187

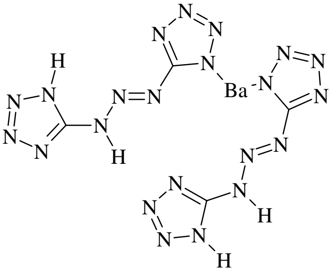
An explosive silver salt is formed.

See Silver buten-3-ynide

See other ALKYNES, PEROXIDISABLE COMPOUNDS

1420. Barium 1,3-di(5-tetrazolyl)triazenide

[ ] **$C_4H_4BaN_{22}$**

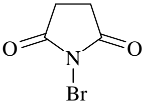


See 1,3-Di(5-tetrazolyl)triazene

See other HIGH-NITROGEN COMPOUNDS, *N*-METAL DERIVATIVES, TETRAZOLES, TRIAZENES

1421. *N*-Bromosuccinimide (1-Bromo-2,5-pyrrolidinedione)

[128-08-5] **$C_4H_4BrNO_2$**



Aniline, or Diallyl sulfide, or Hydrazine hydrate

See other *N*-HALOIMIDES: Alcohols, etc.

Dibenzoyl peroxide, 4-Toluic acid

1. Tcheou, F. K. *et al., J. Chinese Chem. Soc.*, 1950, **17**, 150
2. Mould, R. W., private comm., 1975

Thirtyfold increase in scale of a published method [1] for radical-initiated side-chain bromination of the acid in carbon tetrachloride led to violent reflux and eruption of the flask contents through the condenser [2].

See other HALOGENATION INCIDENTS

Propiononitrile

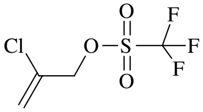
MCA Guide, 1972, 309

After refluxing for 24 hours at 105°C, a mixture exploded, possibly due to dehydrohalogenation of the bromonitrile to acrylonitrile, and polymerisation of the latter.

See other *N*-HALOGEN COMPOUNDS, *N*-HALOIMIDES

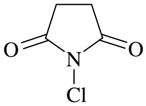
1422. 2-Chloro-2-propenyl trifluoromethanesulfonate

[62861-56-7] **$C_4H_4ClF_3O_3S$**



See entry ALLYL TRIFLUOROMETHANESULFONATES
See other SULFUR ESTERS

1423. *N*-Chlorosuccinimide (1-Chloro-2,5-pyrrolidinedione)
[128-09-6] **$C_4H_4ClNO_2$**



Gustin J.-L., *Chem. Health & Safety*, 2005, **12**(1), 5

Energy of decomposition (in range 160—380°C) measured as 1.61 kJ/g [See Part II cross reference below]. Deflagration may be initiated by contact with steel: use plastic scoops when handling [1].

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alcohols, or Benzylamine

See other *N*-HALOIMIDES: Alcohols, etc.

Dust

Boscott, R. J., private comm., 1968

Smouldering in a stored drum of the chloroimide was attributed to dust contamination.

See other *N*-HALOGEN COMPOUNDS, *N*-HALOIMIDES

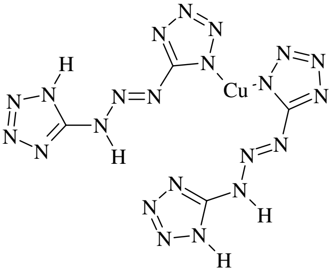
1424. 1,4-Dichloro-2-butyne
[821-10-3] **$C_4H_4Cl_2$**

1. Ford, M. *et al., Chem. Eng. News*, 1972, **50**(3), 67
2. Herberz, T., *Chem. Ber.*, 1952, **85**, 475—482
3. *CHETAH*, 1990, 182 and 188

Preparation of the acetylenic dichloride by conversion of the diol in pyridine with neat thionyl chloride is difficult to control, and hazardous on a large scale. Use of dichloromethane as diluent and operation at —30°C renders the preparation reproducible and safer [1]. During distillation at up to 110°C/7—8 mbar, slight overheating of the residue to 120°C caused explosive decomposition [2]. Sensitive to detonator, sometimes to mechanical shock [3].

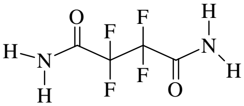
See other HALOACETYLENE DERIVATIVES

1425. Copper(II) 1,3-di(5-tetrazolyl)triazenide
[32061-49-7] **$C_4H_4CuN_{22}$**



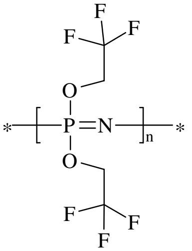
See 1,3-Di(5-tetrazolyl)triazene
See other HIGH-NITROGEN COMPOUNDS, *N*-METAL DERIVATIVES, TETRAZOLES, TRIAZENES

1426. Tetrafluorosuccinamide
[377-37-7] **$C_4H_4F_4N_2O_2$**



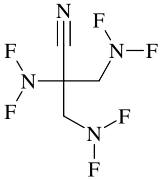
Lithium tetrahydroaluminate
See Lithium terahydroaluminate: Fluoroamides

1427. Poly[bis(2,2,2-trifluoroethoxy)phosphazene]
[28212-50-2] **$(C_4H_4F_6NO_2P)_n$**



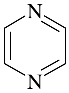
Allcock, H. R. *et al., Macromolecules*, 1974, **7**, 284—290
Sealed tubes containing the linear P═N polymer exploded after heating at 300°C for 24—30 h (or after shorter times at higher temperatures), owing to pressure build-up from formation of the more volatile cyclic tri- and tetra-mers.

1428a. 2-Cyano-1,2,3-tris(difluoroamino)propane
[16176-02-6] **$C_4H_4F_6N_4$**



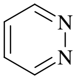
Reed, S. F., *J. Org. Chem.*, 1968, **33**, 1864
The 95% pure material is shock-sensitive.
See other CYANO COMPOUNDS, DIFLUOROAMINO COMPOUNDS

1428b. Pyrazine
[290-37-9] **$C_4H_4N_2$**



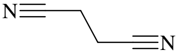
Significantly endothermic ΔH_f° (s) 140 kJ/mole, 1.7 kJ/g. Not a known source of hazard, although pyrazine rings are prominent in many proposed and patented new explosives.
See other ENDOTHERMIC COMPOUNDS

1428c. Pyridazine
[289-80-5] **$C_4H_4N_2$**



Seriously endothermic: ΔH_f° (l) 225 kJ/mole, 2.8 kJ/mole, but not a known source of hazard.
See also Hydrazine
See other ENDOTHERMIC COMPOUNDS

1429. Succinodinitrile (1,4-Butanedinitrile)
[110-61-2] **$C_4H_4N_2$**

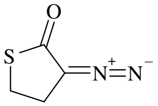


1. Kniess, H., private comm., 1983
2. Berthold, W. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C1—C4, Rugby, IChE, 1983

After vacuum distillation of several t of the nitrile at 150°C, lack of a receiver necessitated hot storage of the product at 80°C for 46 h, and the drainage line blocked with solid. Though the bulk of the material was still liquid, heating to 195°C did not clear the line, and shortly afterwards decomposition occurred. It was subsequently found that the distillation residue had also decomposed at 175°C, 2 h after distillation ended [1]. DTA showed that the nitrile is unusual in that no heat is evolved during the induction period of around 33 h/200°C, or 1.5 h/280°C, and the rapid onset and narrow peak width suggested a self-accelerating decomposition process, with $Q = 700$ J/g. No stabilising additives were found, but addition of 1% of hydrogen cyanide reduced the induction period for the nitrile to 20% of its value, while 1% of potassium cyanide reduced it to 2%. This supports the proposed mechanism of cyanide ion-catalysed decomposition to hydrogen cyanide and acrylonitrile, followed by their simultaneous polymerisation, again by self-accelerating processes. Adiabatic storage tests on 150 g samples gave the same induction period and a decomposition peak of 400°C/40 bar [2].

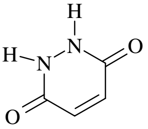
See entry SELF-ACCELERATING REACTIONS
See other CYANO COMPOUNDS, INDUCTION PERIOD INCIDENTS

1430. α-Diazo-γ-thiobutyrolactone
[79472-87-0] **$C_4H_4N_2OS$**



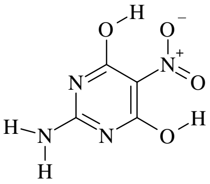
See α-Bromo-γ-thiobutyrolactone
See other DIAZO COMPOUNDS

1431. Maleic hydrazide (1,2-Dihydropyridazine-3,6-dione)
[123-33-1] **$C_4H_4N_2O_2$**



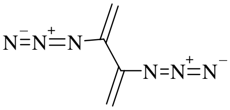
Energy of decomposition (in range 280—300°C) measured as 0.59 kJ/g by DSC, and T_{ait24} was determined as 261°C by adiabatic Dewar tests, with an apparent energy of activation of 257 kJ/mol.

1432. 2-Amino-4,6-dihydroxy-5-nitropyrimidine
[80466-56-4] $C_4H_4N_4O_4$



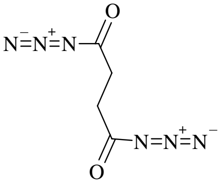
Madeley, J. P., personal communication, 1989
A 200 g sample, prepared by addition of substrate to mixed acid, followed by quenching into water, filtration and washing, decomposed vigorously at a late stage of drying in a vacuum oven, which was pressurised and the seal forced open. This behaviour might have been due to inadequate washing and residual sulfuric acid.
See other C—NITRO COMPOUNDS

1433. 2,3-Diazido-1,3-butadiene
[91686-86-1] $C_4H_4N_6$



Mielsen, C. J. *et al., J. Mol. Struct.*, 1986, **147**, 217—229
Although it is extremely explosive, like other polyunsaturated azides, it was possible to run gaseous electron diffraction and IR spectra at cryogenic temperatures. Sample decomposition occurred during laser Raman spectral determination.
See other DIENES, ENDOTHERMIC COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1434a. Succinoyl diazide
[40428-75-9] $C_4H_4N_6O_2$

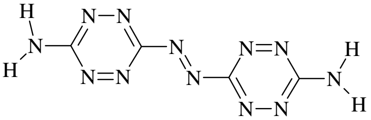


1. Maclaren, J. A., *Chem. & Ind.*, 1971, 3952
2. France, A. D. G. *et al., Chem. & Ind.*, 1962, 2065

This intermediate for the preparation of ethylene diisocyanate exploded violently during isolation [1]. Previously the almost dry solid had exploded violently on stirring with a spatula [2].
See other ACYL AZIDES, FRICTIONAL INITIATION INCIDENTS

1434b. 3,3′-Azobis(6-amino-1,2,4,5-tetrazine) (6,6′-Azobis(1,2,4,5-tetrazin-3-amine))

[303749-95-3] **$C_4H_4N_{12}$**



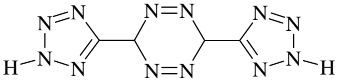
Ali, A.N. *et al., J. Propulsion & Power*, 2004, **20**(1) 120

An *N*-oxide of this (average oxygens per molecule 3.5) has been evaluated as a propellant. It is claimed to have the highest burn rate of any known stable solid.

See other HIGH-NITROGEN COMPOUNDS

1434c. 3,6-Bis(2H-tetrazol-5-yl)-1,4-dihydro-1,2,4,5-tetrazine

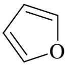
[78697-35-5] **$C_4H_4N_{12}$**



3,6-Bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine

†1435. Furan

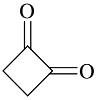
[110-00-9] **C_4H_4O**



See other APROTIC SOLVENTS, PEROXIDISABLE COMPOUNDS

1436. 1,2-Cyclobutanedione

[33689-28-0] **$C_4H_4O_2$**

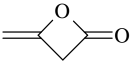


Dennis, J. M. *et al., Org. Synth.*, 1981, **60**, 18—19

The dione must be stored cold and handled out of direct light to prevent polymerisation.

†1437. Diketene (4-Methylene-2-oxetanone)

[674-82-8] **$C_4H_4O_2$**



HCS 1980, 416

1. Vervalin, 1973, 86
2. Zdenek, F. *et al.*, Czech Pat. 156 584, 1975
3. *See entry* PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Diketene residues in a tank trailer awaiting incineration decomposed violently on standing, blew off the dome cover and ignited [1]. The risk of autoignition during the exothermic dimerisation of diketene to dehydroacetic acid is eliminated by operating in a non-flammable solvent [2]. It produces a moderate pressure rise on exothermic decomposition at 125°C [3].

Acids, or Bases, or Sodium acetate

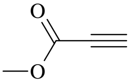
1. *Haz. Chem. Data*, 1975, 136
2. Laboratory Chemical Disposal Co. Ltd., confid. information, 1968
3. Lisochkin, Ya. A. *et al., Chem. Abs.*, 2000, **132**, 226594c

Presence of mineral or Lewis acids, or bases including amines, will catalyse violent polymerisation of this very reactive dimer, accompanied by gas evolution [1]. Sodium acetate is sufficiently basic to cause violent polymerisation at 0.1% concentration when added to diketene at 60°C [2]. A Russian paper describing a tank rupture incident triggered by ingress of acetic acid and pyridine, with suggested precautions against recurrence, is abstracted [3].

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS, POLYMERISATION INCIDENTS

†1438. Methyl propiolate (Methyl propynoate) (Methyl propargylate)

[922-67-8] **$C_4H_4O_2$**



See also Tris(trimethylsilyl)silane: Ethyl propynoate

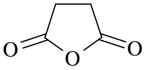
Octakis(trifluorophosphine)dirhodium

See Octakis(trifluorophosphine)dirhodium: Acetylenic esters

See other ACETYLENIC COMPOUNDS

1439. Succinic anhydride

[108-30-5] **$C_4H_4O_3$**



Sodium hydroxide

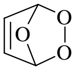
1. Hoekstra, M. C., *Synth. Comm.*, 1984, **14**, 1379—1380
2. Kirk Othmer, 1997, (4th edn.), Vol. 22, 1076

Succinic anhydride is dimerised to 1,6-dioxaspiro [4.4] nonane-2,7-dione by heating with sodium hydroxide. Modification of an existing procedure by adding further sodium hydroxide after the initial reaction led to a severe exothermic reaction after heating for some 30 h which fused the glass flask to the heating mantle, probably at a temperature approaching 550°C. The reason for this was not known [1]. At elevated temperatures and under influence of alkali, succinic acid condenses decarboxylatively beyond the dimeric spiroacetal, sometimes explosively. Contamination of the anhydride with base is to be avoided [2].

See other ACID ANHYDRIDES, GLASS INCIDENTS

1440. 2,3,7-Trioxabicyclo[2,2,1]hept-5-ene

[6824-18-6] **$C_4H_4O_3$**



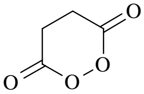
Lorencak, P. *et al., J. Phys. Chem.*, 1989, **93**(6), 2276

This, the ozonide of cyclobutadiene (and also a likely peroxide of furan), may be stored in liquid nitrogen. It can explode with considerable force on warming.

See other CYCLIC PEROXIDES, OZONIDES

1441. 3,6-Dioxo-1,2-dioxane (Succinyl peroxide)

[ ] **$C_4H_4O_4$**



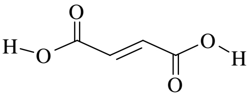
CHETAH, 1990, 183

This cyclic peroxide, readily formed from succinate derivatives and peroxides, is claimed to be more stable than its molecular formula might indicate. It is, however, shock sensitive.

See other CYCLIC PEROXIDES, DIACYL PEROXIDES

1442. Fumaric acid (*trans*-2-Butene-1,4-dioic acid)

[110-17-8] **$C_4H_4O_4$**

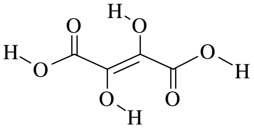


Energy of decomposition (in range 290—340°C) measured as 0.925 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

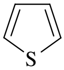
See other ORGANIC ACIDS

1443. Dihydroxymaleic acid (Dihydroxybutenedioic acid)
[526-84-1] **$C_4H_4O_6$**



Axelrod, B., *Chem. Eng. News*, 1955, **33**, 3024
A glass ampoule of the acid exploded during storage at ambient temperature. It is unstable and slowly loses carbon dioxide, even at 4°C.
See other GAS EVOLUTION INCIDENTS, GLASS INCIDENTS, ORGANIC ACIDS

†1444. Thiophene
[110-02-1] **C_4H_4S**



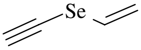
HCS 1980, 899

Modestly endothermic: ΔH_f° (l) 80 kJ/mole

Nitric acid
See Nitric acid: Thiophene

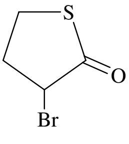
N-Nitrosoacetanilide
See N-Nitrosoacetanilide: Thiophene

1445. Ethynyl vinyl selenide
[101672-11-1] **C_4H_4Se**



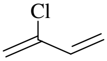
Brandsma, L. *et al., Rec. Trav. Chim.*, 1962, **81**, 539
Distillable at 30—40°C/80 mbar, it decomposes explosively on heating at ambient pressure.
See other ACETYLENIC COMPOUNDS

1446. α-Bromo-γ-thiobutyrolactone (3-Bromo-2-oxotetrahydrothiophene)
[20972-64-9] **C_4H_5BrOS**



Miller, G. A. *et al., J. Org. Chem.*, 1981, **46**, 4751—4753
In the preparation *via* diazotisation and bromination of homocysteine thiolactone, presence of unreacted diazo intermediate led to an explosion during distillation of the product.
See DIAZO COMPOUNDS

†1447. 2-Chloro-1,3-butadiene (Chloroprene)
[126-99-8] **C_4H_5Cl**

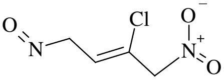


1. Bailey, H. C., in *Oxidation of Organic Compounds-I*, ACS No. 75 (Gould, R. F., Ed.), 138—149, Washington, ACS, 1968
2. Bailey, H. C., private comm., 1974

Chloroprene monomer will autoxidise very rapidly with air, and even at 0°C it produces an unstable peroxide (a mixed 1,2- and 1,4-addition copolymer with oxygen), which effectively will catalyse exothermic polymerisation of the monomer. The kinetics of autoxidation have been studied [1]. It forms ‘popcorn polymer’ at a greater rate than does butadiene [2].
See other DIENES, HALOALKENES, PEROXIDISABLE COMPOUNDS, POLYMERISATION INCIDENTS

Preparative hazard
See 2-Chloro-1-nitro-4-nitroso-2-butene

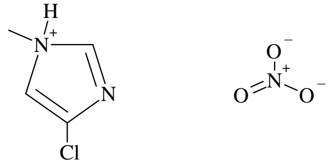
1448. 2-Chloro-1-nitro-4-nitroso-2-butene
[58675-02-8] **$C_4H_5ClN_2O_3$**



Simmons, H. E. *et al., Chem. Eng. News*, 1995, **73**(32), 4
A worker was injured by an explosion when cutting into a “decontaminated” steel pipe removed from a storage tank in a chloroprene plant. The pipe was found to be coated by a deposit of this compound, existing as a dimer. Investigation showed it to be unstable from 80°C, deflagrating with an energy of 2.5 kJ/g (about that of black powder). It is thought it may be capable of true detonation. It was formed by reaction of chloroprene with dinitrogen trioxide, generated during distillation of the chloroprene by decomposition of an ill-defined nitrosated additive used for vapour phase stabilisation against polymerisation reactions. Although originally present at negligible concentration the nitroso-dimer, being very insoluble in chloroprene, accumulated in the pipe. Warning is given that reaction of alkenes with nitrogen oxides, to form similar products, is a general reaction.
See Nitrogen dioxide: Alkenes

1449. 4-Chloro-1-methylimidazolium nitrate

[4897-21-6] (base) **$C_4H_5ClN_3O_3$**



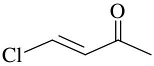
Personal experience

Towards the end of evaporation of a dilute aqueous solution, the residue decomposed violently. Nitrate salts of many organic bases are thermally unstable and should be avoided.

See other OXOSALTS OF NITROGENOUS BASES

1450. 1-Chloro-1-buten-3-one

[7119-27-9] **C_4H_5ClO**



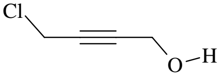
Pohland, A. E. *et al., Chem. Rev.*, 1966, **66**, 164

If prepared from vinyl chloride, this unstable ketone will decompose almost explosively within one day, apparently owing to the presence of some *cis*-isomer.

See related HALOALKENES

1451. 4-Chloro-2-butynol

[13280-07-4] **C_4H_5ClO**



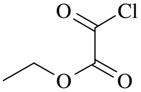
1. Taylor, S. K. *et al., J. Org. Chem.*, 1983, **48**, 595
2. Harmon, D. P. G. *Chem. Brit.* 1998, (7), 19

It exploded during distillation [1]. Another explosion during distillation of a crude sample is reported. It is claimed that there were no previous warnings of the hazard [2].

See other HALOACETYLENE DERIVATIVES

1452. Ethyl oxalyl chloride (Ethyl chloroglyoxylate)

[4755-77-5] **$C_4H_5ClO_3$**



Urben, P. G., Personal experience

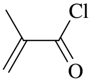
A drum of clear and bright material which had been vacuum distilled pressurised on standing overnight. Investigation revealed a crack in the heat exchanger which had been leaking water into the oxalyl chloride, forming partial anhydrides. These are unstable and decompose to give carbon monoxide and dioxide, other oxalyl halides will behave similarly. On another occasion, a vacuum distillation went suddenly to positive pressure on heating to about 70°C. This was catalysis by traces of iron or aluminium chlorides, which induce break up to, probably, carbon monoxide, carbon dioxide and ethyl chloride.

See Oxalyl dichloride

See other ACYL HALIDES, CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

1453. 2-Methyl-2-propenoyl chloride (Methacryloyl chloride)

[920-46-7] **C_4H_5ClO**



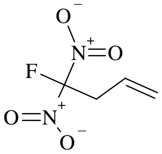
Frazier, J.,*Chem. Eng. News,* 1996, **74**(23), 4

A five year old bottle, originally stabilised with phenothiazine, was found to have polymerised explosively in storage. The resultant black goo was not acidic, suggesting something more complicated than an acrylate polymerisation. It is recommended that this monomer be stored under refrigeration.

See VIOLENT POLYMERISATION

1454. 4-Fluoro-4,4-dinitrobutene

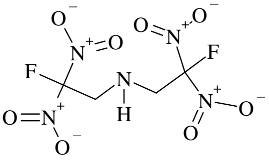
[19273-49-5] **$C_4H_5FN_2O_4$**



See entry FLUORODINITROMETHYL COMPOUNDS, NITROALKENES

1455. Bis(2-fluoro-2,2-dinitroethyl)amine

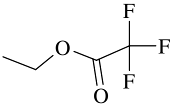
[18139-03-2] **$C_4H_5F_2N_5O_8$**



1. Gilligan, W. H., *J. Org. Chem.*, 1972, **37**, 3947
2. Gilligan, W. H., *J. Chem. Eng. Data*, 1982, **27**, 97—99

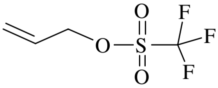
The amine and several derived amides are explosives, and need appropriate care in handling [1]. Several other derivatives, most of them explosive, are prepared and described [2].
See other FLUORODINITROMETHYL COMPOUNDS, ORGANIC BASES

†1456. Ethyl trifluoroacetate
[383-63-1] **$C_4H_5F_3O_2$**



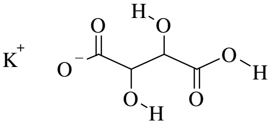
Diethyl succinate, Sodium hydride
See Sodium hydride: Diethyl succinate, etc.

1457. Prop-2-enyl trifluoromethanesulfonate
[41029-45-2] **$C_4H_5F_3O_3S$**



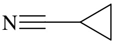
It explodes at 20°C.
See entry ALLYL TRIFLUOROMETHANESULFONATES
See other SULFUR ESTERS

1458. Potassium hydrogen tartrate
[868-14-4] **$C_4H_5KO_6$**



Carbon, Nitrogen oxide
See Nitrogen oxide: Carbon, etc.
See related ORGANIC ACIDS

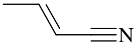
1459. Cyanocyclopropane (Cyclopropanecarbonitrile)
[5500-21-0] **C_4H_5N**



Preparative hazard
See 4-Chlorobutyronitrile: Sodium hydroxide
See other CYANO COMPOUNDS, STRAINED-RING COMPOUNDS

†1460. 1-Cyanopropene (2-Butenonitrile)

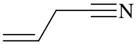
[627-26-9] **C_4H_5N**



See other CYANO COMPOUNDS

†1461. 3-Cyanopropene (3-Butenonitrile)

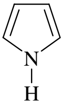
[109-75-1] **C_4H_5N**



See other ALLYL COMPOUNDS, CYANO COMPOUNDS

1462. Pyrrole

[109-97-7] **C_4H_5N**

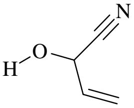


2-Nitrobenzaldehyde

See 2-Nitrobenzaldehyde: Pyrrole

1463. 1-Cyano-2-propen-1-ol (2-Hydroxy-3-butenonitrile)

[5809-59-6] **C_4H_5NO**



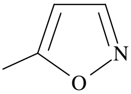
Unpublished information

It shows a strong tendency to exothermic polymerisation of explosive violence in presence of light and air above 25—30°C. Presence of an inhibitor and inert atmosphere are essential for stable storage.

See other CYANO COMPOUNDS

1464. 5-Methylisoxazole

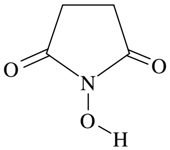
[5765-44-6] **C_4H_5NO**



Sealed samples decompose exothermally above 171°C.

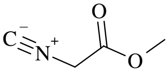
See entry ISOXAZOLES
See other N—O COMPOUNDS

1465. *N*-Hydroxysuccinimide
[6066-82-6] **$C_4H_5NO_3$**



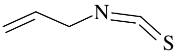
Energy of decomposition (in range 180—370°C) measured as 1.51 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other N—O COMPOUNDS

1466. Methyl isocyanoacetate
[39687-95-1] **$C_4H_5NO_2$**



Heavy metals
Naef, H. *et al.*, private comm., 1983
Crude material prepared in glass on 3 g mol scale was distilled uneventfully at 40°C/0.067 mbar from a bath at 70—80°C. A 30 mol batch prepared in a glass-lined vessel with a stainless steel thermo-probe (and later found to contain 15 ppm of iron) decomposed very violently during distillation at 75°C/13 mbar from a bath at 130°C. Thermal analysis showed that the stability of the methyl (and ethyl) ester was very sensitive to traces of heavy metals (iron, copper, chromium, etc.) and was greatly reduced. Addition of traces of hydrated iron(II) sulfate led to explosive decomposition at 25°C.
See other CATALYTIC IMPURITY INCIDENTS
See related CYANO COMPOUNDS

1467. Allyl isothiocyanate (3-Isothiocyanatopropene)
[57-06-7] **C_4H_5NS**



Anon., *Ind. Eng. Chem. (News Ed.)*, 1941, **19**, 1408
A routine preparation by interaction of allyl chloride and sodium thiocyanate in an autoclave at 5.5 bar exploded violently at the end of the reaction. Peroxides were not present or involved and no other cause could be found, but extensive decomposition

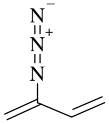
occurred when allyl isothiocyanate was heated to 250°C in glass ampoules. Exothermic polymerisation seems a likely possibility.

See other ALLYL COMPOUNDS

See related CYANO COMPOUNDS, ORGANIC ISOCYANATES

1468. 2-Azido-1,3-butadiene

[91686-88-3] **$C_4H_5N_3$**



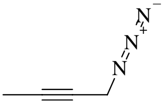
Schel, S. A. *et al., J. Mol. Struct.*, 1986, **147**(3—4), 203—215

Although it is highly explosive, like other polyunsaturated azides, it was possible to record spectral data under the following conditions: gaseous electron diffraction; IR spectra of matrix-isolated species in argon at 15°K; of amorphous and crystalline solids at 90°K and Raman spectra of the liquid at 240°K.

See other DIENES, ENDOTHERMIC COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1469. Azido-2-butyne

[105643-77-4] **$C_4H_5N_3$**



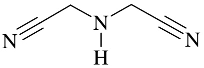
Nielsen, C. J. *et al., J. Mol. Struct.*, 1987, **16**(1—2), 41—56

Precautions appropriate to a potentially explosive compound were observed during synthesis and handling. Electron diffraction studies on the vapour, and IR, NMR and Raman spectral studies on the vapour, liquid and solid (—183°C) phases were effected without incident.

See other ACETYLENIC COMPOUNDS, ENDOTHERMIC COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1470. Iminobisacetonitrile

[628-87-5] **$C_4H_5N_3$**



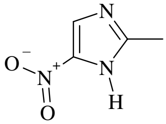
Anon., *Loss. Prev. Bull.*, 1993, (109), 7

Iminobisacetonitrile crystallised in a holding tank of a production plant. Cleaning was by filling with water and heating to dissolve the nitrile. It was heated to a supposed 75°C. An hour later the tank exploded causing severe structural damage. The pyrometer used to measure the temperature was found inaccurate. The nitrile decomposes exothermically from perhaps as low as 70°C in alkaline water (135°C dry) to a variety of products including HCN.

See other CYANO COMPOUNDS

1471. 2-Methyl-4-nitroimidazole

[696-23-1] **$C_4H_5N_3O_2$**



Zmojdzin, A. *et al.*, Brit. Pat. 1 418 538, 1974

2-Methylimidazole is difficult to nitrate, and use of conventional reagents under forcing conditions (excess sulfuric/nitric acids, high temperature) involves a high risk of cleavage and violent runaway oxidation. A new and safe process involves the use of nitration liquor from a previous batch (and optional use of excess nitric acid), both of which moderate the nitration reaction, in conjunction with balancing amounts of sulfuric acid, which tends to accelerate the nitration of 2-methylimidazole. Accurate control of the highly exothermic reaction is readily effected.

See other NITRATION INCIDENTS

Nitric acid, Sulfuric acid

Zmojdzin, A. *et al.*, Fr. Demande 2 220 523, 1974

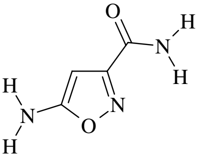
The danger of explosion during further nitration with nitrating acid is eliminated by addition of excess nitric acid as the reaction proceeds.

See NITRATION INCIDENTS

See related NITROARYL COMPOUNDS

1472. 5-Aminoisoxazole-3-carbonamide

[3445-52-1] **$C_4H_5N_3O_2$**



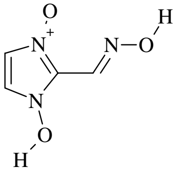
Sealed samples decompose exothermally above 155°C.

See entry ISOXAZOLES

See other N—O COMPOUNDS

1473. 1-Hydroxyimidazole-2-carboxaldoxime 3-oxide

[53967-34-3] **$C_4H_5N_3O_3$**



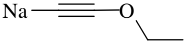
Hayes, K. J., *J. Heterocycl. Chem.*, 1974, **11**, 615

It is an explosive solid, containing three types of N—O bonds.

See other N—O COMPOUNDS, OXIMES

1474. Sodium ethoxyacetylide

[73506-39-5] **C_4H_5NaO**



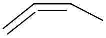
1. Jones, E. R. H. *et al., Org. Synth.*, 1963, Coll. Vol. 4, 405
2. Brandsma, 1971, 120

It is extremely pyrophoric, apparently even at —70°C [1], and may explode after prolonged contact with air [2].

See other METAL ACETYLIDES, PEROXIDISABLE COMPOUNDS

†1475. 1,2-Butadiene

[590-19-2] **C_4H_6**



Highly endothermic, ΔH_f° (g) +165.5 kJ/mol, 3.06 kJ/g.

Cyclopentadiene (or its dimer)

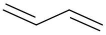
Donike, W., Ger. Offen. DE 3 617 461, 1987 (*Chem. Abs.*, 1988, **109**, 210597)

In the Diels-Alder condensation of the 2 neat endothermic dienes to give 5-ethylidene- and 5-methyl-6-methylene-bicyclo[2.2.1]hept-2-ene, there is a serious risk of explosive decomposition arising from local overheating of the reactor walls. This hazard is eliminated by the presence of various hydrocarbons and their mixtures as diluents.

See other DIENES, ENDOTHERMIC COMPOUNDS

†1476. 1,3-Butadiene

[106-99-0] **C_4H_6**



(*MCA SD-55*, 1954); *FPA H63*, 1977; *HCS 1980*, 223 (cylinders); *RSC Lab. Hazards Data Sheet No. 45*, 1986

1. Scott, D. A., *Chem. Eng. News*, 1940, **18**, 404
2. Hendry, D. G. *et al., Ind. Eng. Chem., Prod. Res. Dev.*, 1968, **7**, 136, 1145
3. Mayo, F. R. *et al., Prog. Rept. No. 40*, Sept. 1971, Stamford Res. Inst. Project PRC-6217
4. Keister, R. G. *et al., Loss Prev.*, 1971, **5**, 69
5. Penkina, O. M. *et al., Chem. Abs.*, 1975, **83**, 29457
6. Bailey, H. C., private comm., 1974
7. Miller, G. H. *et al., J. Polymer Sci. C*, 1964, 1109—1115
8. Vervalin, 1964, 335—338, 358—359
9. Harmon, 1974, 2.5—2.6
10. Alexander, D. S., *Ind. Eng. Chem.*, 1959, **51**, 733—738
11. Thayer, A., *Chem. Eng. News*, 2000, **78**(17), 10
12. Fisher, H. G. *et al., Int. Symp. Runaway React., Pressure Relief Des., Effluent Handl.*,1998, 445
13. www.acusafe.com/Newsletter, 2000(May)
14. Levin, M. E. *et al., J. Haz. Mat.*, 2004, **115**(1-3), 71

Solid butadiene at below —113°C will absorb enough oxygen at reduced pressure to make it explode violently when allowed to melt. The peroxides formed on long contact with air are explosives sensitive to heat or shock, but may also initiate polymerisation [1]. The hazards associated with peroxidation of butadiene are closely related to the fact that the polyperoxide is insoluble in butadiene and progressively separates. If local concentrations build up, self-heating from the (initially slow) spontaneous decomposition begins, and when a large enough mass of peroxide accumulates, explosion occurs. Critical mass at 27°C is a 9 cm sphere; the size decreases rapidly with increasing temperature [2]. Although isoprene and styrene also readily peroxidise, the peroxides are soluble in the monomers, and the degree of hazard is correspondingly less [3].

Butadiene is rather endothermic (ΔH_f° (g)+111.9 kJ/mol, 2.07 kJ/g) and will decompose explosively if heated under pressure at 30—40°C/min to exceed critical temperatures of 200—324°C and critical pressures of 1.0—1.2 kbar simultaneously [4]. A later study of the explosion properties of butadiene at elevated temperatures and pressures has been published (but title only translated) [5]. Phenolic antioxidants (e.g. *tert*-butylcatechol at 0.02 wt.%) are effective in stabilising butadiene against autoxidation in clean storage at moderate ambient temperatures. The presence of rust and/or water in steel storage cylinders rapidly consumes the antioxidant [6]. Further study of the hazards of butadiene, reported in a review, shows a non-radical dimerisation and trimerisation becoming significant at somewhat above ambient temperature. These reactions are not inhibited by radical inhibitors, but may heat bulk butadiene to a temperature at which the more dangerous radical polymerisation and later polymer decomposition set in. temperatures of 600C and pressures over 130 bar are attainable [12]. In prolonged storage, butadiene will (even when very pure and in sealed glass containers) produce 'popcorn' polymer [7]. Growth of this involves continued diffusion of monomer into an existing polymeric matrix which continues to increase in bulk. The expansion eventually may rupture the container [6]. Isolated popcorn polymer retains the capacity to react with free butadiene at no very elevated temperature [14]. An account of a popcorn polymerisation which propagated from an uncontrolled reactor, blocking lines and bursting a storage tank [11]. Case histories of two industrial explosions involving peroxide formation with air have been detailed [8], and the literature relating to violent polymerisation of butadiene has been reviewed [9]. A detailed account of the experimental investigation following a large-scale explosion in 1951 of a partially full 159 m^3 butadiene storage vessel is given. The involvement of peroxide formation in the explosion was established, as was the effectiveness of the presence of aqueous sodium hydroxide in destroying peroxide and preventing explosion [10]. Serious accidents associated with spontaneous polymerisation of butadiene, and possibly popcorn, continue to happen [13].

See Poly(1,3-butadiene peroxide): Butadiene

See entry POLYMERISATION INCIDENTS, VIOLENT POLYMERISATION

See other GLASS INCIDENTS, PEROXIDATION INCIDENTS, SELF-HEATING AND IGNITION INCIDENTS

Aluminium tetrahydroborate

See Aluminium tetrahydroborate: Alkenes, etc.

Boron trifluoride etherate, Phenol

MCA Case History No. 790

The hydrocarbon—phenol reaction, catalysed by the etherate, was being run in petroleum ether solution in a sealed pressure bottle. The bottle burst, possibly owing to exothermic polymerisation of the diene.

Buten-3-yne

See Buten-3-yne: 1,3-Butadiene

Cobalt

See reference 7 above

Crotonaldehyde

See Crotonaldehyde: Butadiene

Ethanol, Iodine, Mercury oxide

See 2-Ethoxy-1-iodo-3-butene

Other reactants

Yoshida, 1980, 296

MRH values calculated for 13 combinations with oxidants are given.

Oxides of nitrogen, Oxygen MRH Nitrogen oxide 8.74/85

Vervalin, 1973, 63—65

An explosion and fire occurred in the pipework of a vessel in which dilute butadiene was stored under an ‘inert’ atmosphere, generated by the combustion of fuel gas in a limited air supply. The ‘inert’ gas, which contained up to 1.8% of oxygen and traces of oxides of nitrogen, reacted in the vapour phase over an extended period to produce concentrations of gummy material containing up to 64% of butadiene peroxide and

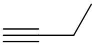
4.2% of a butadiene—nitrogen oxide complex. The deposits eventually decomposed explosively.
See Nitrogen oxide: Dienes, Oxygen

Oxygen
MCA Case History No. 303
A leaking valve allowed butadiene to accumulate in a pipeline exposed to an inerting gas containing up to 2% of oxygen. Peroxide formed and initiated ‘popcorn’ polymerisation which burst the pipeline.
See reference 6 above

Sodium nitrite
See Sodium nitrite: 1,3-Butadiene
See other DIENES, ENDOTHERMIC COMPOUNDS, PEROXIDISABLE COMPOUNDS

†1477. 1-Butyne

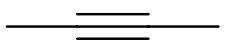
[107-00-6] **C_4H_6**



Highly endothermic (ΔH_f° (g) +166.1 kJ/mol, 3.07 kJ/g).
See other ALKYNES, ENDOTHERMIC COMPOUNDS

†1478. 2-Butyne

[503-17-3] **C_4H_6**

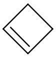


HCS 1980, 253

Highly endothermic (ΔH_f° (g) +148.0 kJ/mol, 2.74 kJ/g).
See other ALKYNES, ENDOTHERMIC COMPOUNDS

†1479. Cyclobutene

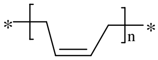
[822-35-5] **C_4H_6**



See other ALKENES

1480. *cis*-Poly(butadiene)

[9003-17-2] **$(C_4H_6)_n$**



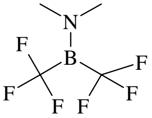
Sedov, V. V. *et al., Chem. Abs.*, 1976, **85**, 109747

Stereoregular *cis*-poly(butadiene) compositions may explode when heated at 337—427°C/1—0.01 μbar, presumably owing to exothermic cyclisation.

See related DIENES

1481. Dimethylaminobis(trifluoromethyl)borane (*N,N*-Dimethyl-1,1-bis(trifluoromethyl)boranamine)

[105224-90-6] **$C_4H_6BF_6N$**



Primary alkynes

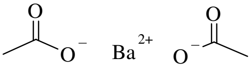
Bürger, H. *et al., Main Group Met. Chem.,* 1995, **18**(5), 235

The adducts of primary alkynes with the borane may explode when heated to 90°C.

See other ACETYLENIC COMPOUNDS

1482. Barium acetate

[543-80-6] **$C_4H_6BaO_4$**



Copper(II) oxide, Yttrium oxide

1. Fleischer, N., *Chem. Eng. News*, 1988, **66**(15), 2
2. Author's comments
3. Castrillon, J., *Chem. Eng. News*, 1988, **66**(25), 2

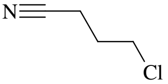
A pelleted mixture containing barium acetate, copper(II) oxide and yttrium oxide, 3 g in all in a quartz tube, was heated in a furnace, and a small explosion occurred during the early stages, 'from formation of pyrolysis products'. It was suggested that the tube should in future be purged, preferably with an oxygen-containing gas [1]. This suggestion is hazardous, however, as the pyrolysis product is acetone. Only inert gas should be used for purging [2]. Pyrolysis of barium acetate gives high yields of acetone, and is catalysed by the metal oxides present in the mixture [3].

See Cadmium propionate

See other HEAVY METAL DERIVATIVES

1483. 4-Chlorobutyronitrile (4-Chlorobutanonitrile)

[628-20-6] **C_4H_6ClN**



Sodium hydroxide

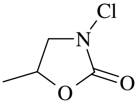
Brogli, F. *et al., Runaway Reactions*, 1981, Paper 3/M, 5—6, 10

Unstable plant-scale operation in the catalysed cyclisation by sodium hydroxide to cyclopropanecarbonitrile was investigated using a bench scale calorimeter. Crust formation on the reactor wall, which caused the erratic operation, was eliminated by using liquid alkali instead of solid.

See other CYANO COMPOUNDS

1484. *N*-Chloro-5-methyl-2-oxazolidinone

[25480-76-6] **$C_4H_6ClNO_2$**



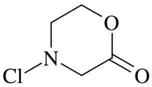
Walles, W. E., US Pat. 3 850 920, 1974

It exploded at 160°C.

See other *N*-HALOGEN COMPOUNDS

1485. *N*-Chloro-3-morpholinone

[33744-03-5] **$C_4H_6ClNO_2$**



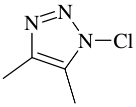
Walles, W. E., US Pat 3 850 920, 1974

It exploded at 115°C.

See other *N*-HALOGEN COMPOUNDS

1486. *N*-Chloro-4,5-dimethyltriazole

[72040-09-6] **$C_4H_6ClN_3$**



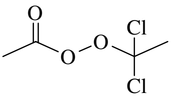
Gallagher, T. C. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 420

The solid (or a concentrated solution) decomposes vigorously on standing at ambient temperature and needs careful handling.

See other *N*-HALOGEN COMPOUNDS, TRIAZOLES

1487. 1,1-Dichloroethyl peroxyacetate

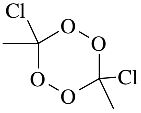
[59183-18-5] **$C_4H_6Cl_2O_3$**



Griesbaum, K. *et al., J. Amer. Chem. Soc.*, 1976, **98**, 2880
A friction- and heat-sensitive viscous liquid, it exploded violently during attempted injection into a gas chromatograph.
See other PEROXYESTERS

1488. 3,6-Dichloro-3,6-dimethyltetraoxane

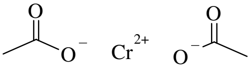
[59183-17-4] **$C_4H_6Cl_2O_4$**



Griesbaum, K. *et al., J. Amer. Chem. Soc.*, 1976, **98**, 2880
Extremely sensitive to shock, heat or minor friction, it has exploded very violently when touched with a glass rod or spatula.
See other CYCLIC PEROXIDES

1489. Chromium(II) acetate

[628-52-4] **$C_4H_6CrO_4$**

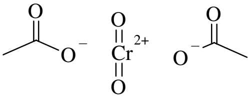


1. Ocone, L. R. *et al., Inorg. Synth.*, 1966, **8**, 129—131
2. Young, G. C., *J. Chem. Educ.*, 1988, **65**, 918—919

The anhydrous salt is pyrophoric in air, or chars slowly in lower oxygen concentrations [1]. A safe and convenient synthesis of the dimeric monohydrate is described [2].
See Bis(2,4-pentanedionato)chromium
See other PYROPHORIC MATERIALS

1490. Chromyl acetate

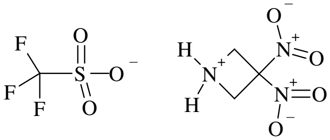
[4112-22-5] **$C_4H_6CrO_6$**



Preparative hazard
See Chromium trioxide: Acetic anhydride
See other OXIDANTS

1491. 3,3-Dinitroazetidinium trifluoromethanesulfonate

[ ] **$C_4H_6F_3N_3O_7S$**



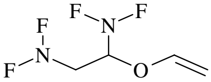
Hiskey, M. A. *et al., J. Heterocycl. Chem.,* 1992, **29**(7), 1855

The *gem*-dinitro compound is shock sensitive, deflagrating under a heavy hammer blow.

See related POLYNITROALKYL COMPOUNDS

1492. 1,2-Bis(difluoroamino)ethyl vinyl ether

[13084-45-2] **$C_4H_6F_4N_2O$**



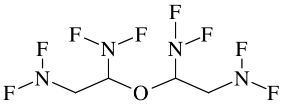
Reed, S. F., *J. Org. Chem.*, 1967, **32**, 2894

It is slightly less impact-sensitive than glyceryl nitrate.

See other DIFLUOROAMINO COMPOUNDS

1493. Di-1,2-bis(difluoroaminoethyl) ether

[13084-46-3] **$C_4H_6F_8N_4O$**



Reed, S. F., *J. Org. Chem.*, 1967, **32**, 2894

It is slightly more impact-sensitive than glyceryl nitrate.

See other DIFLUOROAMINO COMPOUNDS

1494. Divinylmagnesium

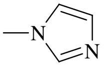
[6928-74-1] **C_4H_6Mg**

Houben-Weyl, 1973, Vol. 13.2a, 203

The solid may ignite in air.

See related ALKYLMETALS

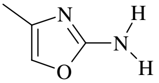
1495. 1-Methylimidazole
[616-47-7] **$C_4H_6N_2$**



Osmium(VIII) oxide

See Osmium(VIII) oxide: 1-Methylimidazole

1496. 2-Amino-4-methyloxazole
[35629-70-0] **$C_4H_6N_2O$**

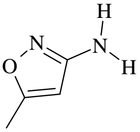


Hydrogen peroxide

See Hydrogen peroxide: 2-Amino-4-methyloxazole

See related ISOXAZOLES

1497. 3-Amino-5-methylisoxazole
[1072-67-9] **$C_4H_6N_2O$**



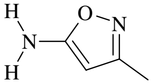
Cardillo, P., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 46—48; *Chem. Eng. News*, 1988, **66**(1), 4

The molten compound (100 kg) at 80°C was put into a 200 l drum for storage, but the closed drum exploded after 2 h. Analysis showed the presence of 5-amino-3-methylisoxazole as the main impurity. Thermal stability of the title compound, of the isomeric impurity, and of a mixture of the former with 5% of the latter was investigated by DSC and ARC. Very high self-heating rates were seen, and while the pure 3-amino compound decomposed from 140—160°C, the impure mixture and the prepared mixture of isomers started to decompose at 62°C, the decomposition exotherms being above 1.9 kJ/g in all cases, accompanied by gas evolution. The rapid rate of pressure rise and the final pressure (above 170 bar) which were observed explain the violent bursting of the drum of exothermically decomposing material. The thermal stability of the isomeric 5-amino-3-methylisoxazole was lower than that of the title compound (though the decomposition exotherm was lower at 1.42 kJ/g), and the presence of a few % of the 5-amino compound led to violent exothermic decomposition of the molten compound at 80°C.

See entry ISOXAZOLES

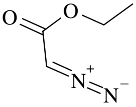
See other N—O COMPOUNDS

1498. 5-Amino-3-methylisoxazole
[14678-02-5] **$C_4H_6N_2O$**



See 3-Amino-5-methylisoxazole (next above)
See entry ISOXAZOLES
See other N—O COMPOUNDS

1499. Ethyl diazoacetate
[623-73-4] **$C_4H_6N_2O_2$**

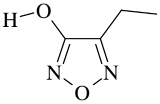


1. Searle, N. E., *Org. Synth.*, 1962, Coll. Vol. 4, 426
2. Soos, R. *et al., Chem. Abs.*, 1984, **101**, 230032
3. Clark, J. D. *et al., Proc. 27th NATAS Annu. Conf. Therm. Anal. Appl.*, 1999, 119; *28th ibid.*, 2000, 346
4. Clark, J. D. *et al., Thermochim. Acta*, 2002, **386**(1), 73

It is explosive, and distillation, even under reduced pressure as described, may be dangerous [1]. A Hungarian patent describes a safe procedure for *in-situ* generation of the ester, azeotropic dehydration and subsequent metal-catalysed reaction with 1,3-dienes to give alkyl cyclopropanecarboxylates [2]. A calorimetric study and consequent engineering considerations for industrial scale use of solutions of this reagent have been described [3]. It is claimed it does not detonate [4].

Tris(dimethylamino)antimony
Krommes, P. *et al., J. Organomet. Chem.*, 1975, **97**, 63, 65
Interaction at ambient temperature, either initially or on warming from —20°C or below, becomes explosively violent.
See other DIAZO COMPOUNDS

1500. 3-Ethyl-4-hydroxy-1,2,5-oxadiazole (4-Ethyl-3-furazanone)
[34529-29-8] **$C_4H_6N_2O_2$**



Sodium hydroxide
Barker, M. D., *Chem. & Ind.*, 1971, 1234

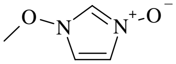
The sodium salt obtained by vacuum evaporation at 50°C of an aqueous alcoholic mixture of the above ingredients exploded violently when disturbed.

See other N—O COMPOUNDS

See related FURAZAN N-OXIDES

1501. 1-Methoxyimidazole *N*-oxide

[90052-22-5] **$C_4H_6N_2O_2$**



Flynn, A. P., *Chem. Brit.*, 1984, **20**, 30

Attempted removal of water from a 3 g sample of the hydrate by vacuum distillation at 150—180°C/0.027 mbar caused a violent explosion as distillation started. DSC examination showed a large decomposition exotherm at 140—180°C.

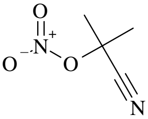
See 1-Methoxy-3,4,5-trimethylpyrazole *N*-oxide

See also 1-Hydroxyimidazole *N*-oxide

See other *N*-OXIDES

1502. 2-Cyano-2-propyl nitrate (2-Methyl-2-nitrooxypropanonitrile) (Acetone cyanohydrin nitrate)

[40561-27-1] **$C_4H_6N_2O_3$**



Freeman, J. P., *Org. Synth.* Coll. Vol. 5, 841

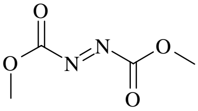
It is a moderately explosive material of moderate impact-sensitivity. Use of a safety shield is advised for distillation.

See NITRATING AGENTS

See other ALKYL NITRATES, CYANO COMPOUNDS, N—O COMPOUNDS

1504. Dimethyl azoformate (Dimethyl diazenedicarboxylate)

[2446-84-6] **$C_4H_6N_2O_4$**



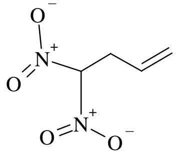
1. US Pat. 3 347 845, 1967
2. Kauer, J. C., *Org. Synth.*, 1962, Coll. Vol. 4, 412
3. Young, J. A., private communication, 1993
4. Diels, O. *et al., Berichte*, 1913, **46**, 2006

It is shock-sensitive [1]. An undergraduate student was preparing a 200 g batch following the Organic Syntheses procedure [2]. The first stage quality is believed to have been poor. The final product exploded during vacuum distillation, costing her the sight of an eye [3]. Since the first man to describe it compared it with guncotton, when heated under slight confinement [4], it might be considered unsuitable for undergraduates. The editor suspects that hydrazoic acid reported as an hydrolysis product may indicate that procedure [2] can produce methyl azidoformate as a byproduct. Diels [4] also demonstrated formation of another very unstable compound from its further reaction with nitric acid, which is the oxidant used in the second stage of preparation [2].

See Diethyl azoformate
See Ethyl azidoformate
See other AZO COMPOUNDS

1505. 1,1-Dinitro-3-butene

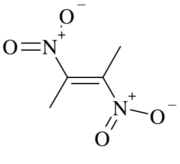
[10229-09-1] **$C_4H_6N_2O_4$**



Witucki, E. F. *et al., J. Org. Chem.*, 1972, **37**, 152
A fume-off during distillation of this compound (b.p., 63—65°C/2 mbar) illustrates the inherent instabilty of this type of compound.
See other NITROALKENES, POLYNITROALKYL COMPOUNDS

1506. 2,3-Dinitro-2-butene

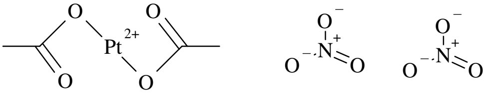
[28103-68-6] **$C_4H_6N_2O_4$**



Bisgrove, D. E. *et al., Org. Synth.*, 1962, Coll. Vol. 4, 374
Only one explosion has been recorded during vacuum distillation at 135°C/14 mbar.
See other NITROALKENES, POLYNITROALKYL COMPOUNDS

1507. Diacetatoplatinum(II) nitrate

[ ] $C_4H_6N_2O_{10}Pt$



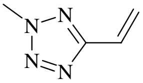
Preparative hazard

See Nitric acid: Acetic acid, etc.

See other PLATINUM COMPOUNDS

1508. 2-Methyl-5-vinyltetrazole

[15284-39-6] $C_4H_6N_4$



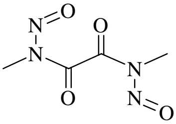
Aluminium hydride

See Aluminium hydride: Tetrazole derivatives

See other TETRAZOLES

1509. *N,N′*-Dimethyl-*N,N′*-dinitrosooxamide

[7601-87-8] $C_4H_6N_4O_4$



Preussmann, R., *Angew. Chem.*, 1963, **75**, 642

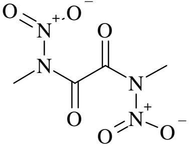
Removal of the solvent carbon tetrachloride (in which nitrosation had been effected) at ambient, rather than reduced, pressure caused a violent explosion at the end of distillation. Lowest possible temperatures should be maintained in the preparation. Other precursors seem more suitable as sources of diazomethane.

See Diazomethane

See other NITROSO COMPOUNDS

1510. *N,N′*-Dimethyl-*N,N′*-dinitrooxamide

[14760-99-7] $C_4H_6N_4O_6$

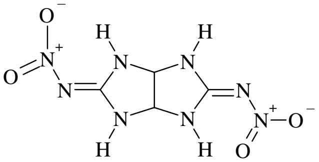


Allenby, O. C. W. *et al., Can. J. Res.*, 1947, **25B**, 295—300

It is an explosive.
See other N—NITRO COMPOUNDS

1511. Octahydro-2,5-bis(nitroimino)imidazo[4,5-*d*]imidazole (1.3a,4,6a-Tetrahydro-*N,N′*-dinitroimidazo[4,5-*d*]imidazole-2,5-diamine)

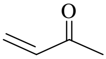
[139394-51-7] **$C_4H_6N_8O_4$**



Dagley, I. J. *et al., J. Energ. Mater.*, 1995, **13**(1&2), 35
This nitroguanidine analogue is more sensitive than RDX by the drop-weight impact test.
See other N—NITRO COMPOUNDS

†1512. 1-Buten-3-one (Methyl vinyl ketone)

[78-94-4] **C_4H_6O**



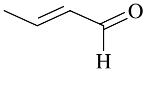
HCS 1980, 665

Haz. Chem. Data, 1975, 207
The uninhibited monomer polymerises on exposure to heat or sunlight. The inhibited monomer may also polymerise if heated sufficiently (by exposure to fire) and lead to rupture of the containing vessel.
See other POLYMERISATION INCIDENTS

Other reactants
Yoshida, 1980, 368
MRH values calculated for 13 combinations with oxidants are given.

†1513. Crotonaldehyde (2-Butenal)

[4170-30-3] **C_4H_6O**



HCS 1980, 330

Butadiene
1. Greenlee, K. W., *Chem. Eng. News*, 1948, **26**, 1985
2. Hanson, E. S., *Chem. Eng. News*, 1948, **26**, 2551
3. Watson, K. M., *Ind. Eng. Chem.*, 1943, **35**, 398

An autoclave without a bursting disk and containing the two poorly mixed reactants was wrecked by a violent explosion which occurred on heating the autoclave to 180°C [1]. This was attributed to not allowing sufficient free space for liquid expansion to occur [2]. The need to calculate separate reactant volumes under reaction conditions for all autoclave preparations is stressed [3].
See 1,3-Butadiene

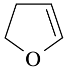
Ethyl acetoacetate

Soriano, D. S. *et al., J. Chem. Educ.*, 1988, **65**, 637
A procedure using a phase-transfer catalyst is employed to prevent the rapid polymerisation of crotonaldehyde during the Robinson annulation reaction.
See related POLYMERISATION INCIDENTS

Nitric acid

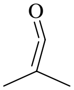
See Nitric acid: Crotonaldehyde
See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

†1514. 2,3-Dihydrofuran
[1191-99-7] **C_4H_6O**



See other PEROXIDISABLE COMPOUNDS

1515. Dimethylketene (2-Methyl-1-propene-1-one)
[598-26-5] **C_4H_6O**



1. Smith, G. W. *et al., Org. Synth.*, 1962, Coll. Vol. 4, 348
2. Staudinger, H., *Ber.*, 1925, **58**, 1079—1080

Dimethylketene rapidly forms an extremely explosive peroxide when exposed to air at ambient temperatures. Drops of solution allowed to evaporate may explode. Inert atmosphere should be maintained above the monomer [1]. The peroxide is polymeric and very sensitive, exploding on friction at —80°C. Higher homologues are very unstable and unisolable [2].
See other FRICTIONAL INITIATION INCIDENTS

Oxygen

See Poly(peroxyisobutyrolactone)
See other POLYPEROXIDES

†1516. Divinyl ether (1,1′-Oxybisethene)

[109-93-3] **C_4H_6O**

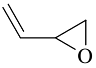
Anon., *Chemist & Druggist*, 1947, **157**, 258
The presence of *N*-phenyl-1-naphthylamine as inhibitor considerably reduces the development of peroxide in the ether.

Nitric acid

See Nitric acid: Divinyl ether
See other PEROXIDISABLE COMPOUNDS

†1517. 3,4-Epoxybutene (Vinyloxirane)

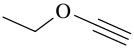
[930-22-3] **C_4H_6O**



See other 1,2-EPOXIDES

†1518. Ethoxyacetylene (Ethoxyethyne)

[927-80-0] **C_4H_6O**



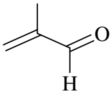
Jacobs, T. L. *et al., J. Amer. Chem. Soc.*, 1942, **64**, 223
Small samples rapidly heated in sealed tubes to around 100°C exploded.

Ethylmagnesium iodide

See Ethylmagnesium iodide: Ethoxyacetylene
See other ACETYLENIC COMPOUNDS

†1519. Methacrylaldehyde (2-Methylpropenal)

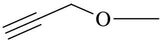
[78-85-3] **C_4H_6O**



See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

1520. 3-Methoxypropyne (Methyl propargyl ether)

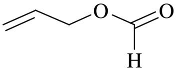
[627-41-8] **C_4H_6O**



Brandsma, 1971, 13
It explodes on distillation at its atmospheric b.p., 61°C.
See other ACETYLENIC COMPOUNDS

†1521. Allyl formate (3-Propenyl methanoate)

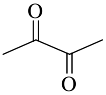
[1838-59-1] **$C_4H_6O_2$**



See other ALLYL COMPOUNDS

†1522. Butane-2,3-dione

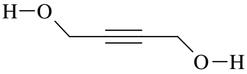
[431-03-8] **$C_4H_6O_2$**



HCS 1980, 228

1523. 2-Butyne-1,4-diol

[110-65-6] **$C_4H_6O_2$**

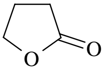


Alkalies, or Halide salts, or Mercury salts and acids

Kirk-Othmer, 1960, Suppl. Vol. 2, 45
The pure diol may be distilled unchanged, but traces of alkali or alkaline earth hydroxides or halides may cause explosive decomposition during distillation. In presence of strong acids, mercury salts may cause violent decomposition of the diol.
See other ACETYLENIC COMPOUNDS, CATALYTIC IMPURITY INCIDENTS

1524a. Butyrolactone (2(3*H*)-Dihydrofuranone)

[96-48-0] **$C_4H_6O_2$**



Butanol, 2,4-Dichlorophenol, Sodium hydroxide

Anon., *CISHC Chem. Safety Summ.*, 1977, **48**, 3

In an altered process to prepare 2,4-dichlorophenoxybutyric acid, the lactone was added to the other components, and soon after, the reaction temperature reached 165°C, higher than the usual 160°C. Application of cooling failed to check the thermal runaway, and soon after reaching 180°C the vessel began to fail and an explosion and fire occurred.

See other RUNAWAY REACTIONS

†1524b. 1,2:3,4-Diepoxybutane

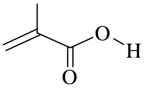
[298-18-0] **$C_4H_6O_2$**

$C_4H_6O_2$

See other 1,2-EPOXIDES

1525. Methacrylic acid (2-Methylpropenoic acid)

[79-41-4] **$C_4H_6O_2$**



1. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 34
2. Bond, J., *Loss Prev. Bull.*, 1991, **101**, 1
3. Anderson, S. E. *et al., Plant/Oper. Progress*, 1992, **11**(3), 151
4. Nicolson, A., *Plant/Oper. Progress.*, 1991, **10**(3), 171

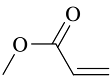
A drum of the uninhibited acid (m.p., 16°C) which had been stored outside under winter conditions was transferred into a warm room to liquefy the acid. Later, exothermic polymerisation led to bulging of the drum and leakage of the acid vapour [1]. A more serious accident involved a railtank of acid-washed crude technical methacrylic acid (liable to throw down a dilute H_2SO_4 layer) which exploded, throwing debris 300 metres, some 20 hrs after a pressure relief valve was seen to lift, despite being sprayed with water meanwhile [2,3]. It was shipped in unlined steel without corrosion tests because that had previously been used for purified inhibited product and it contained negligible stabiliser. A study of the complex interactions of oxygen (inhibitory at low but not at high concentrations) and stabilisers is reported [3]. Phenothiazine seems a better inhibitor than the usual phenols.

See Acrylic acid

See other CORROSION INCIDENTS, CORROSION INCIDENTS, ORGANIC ACIDS, POLYMERISATION INCIDENTS

†1526. Methyl acrylate (Methyl propenoate)

[96-33-3] **$C_4H_6O_2$**



(*MCA SD-79*, 1960); *HCS 1980*, 634

1. *MCA Case History No. 2033*
2. Harmon, 1974, 2.11
3. *See entry* SELF-ACCELERATING REACTIONS

A 4 l glass bottle of the ester (sealed and partly polymerised old stock) exploded several hours after being brought from storage into a laboratory. An inhibitor had originally been present, but could have been consumed during prolonged storage, and peroxides may have initiated exothermic polymerisation of the remaining monomer [1]. The monomer is normally stored and handled inhibited and at below 10°C, but not under inert atmosphere, because traces of oxygen are essential to the inhibition process [2]. DSC investigation showed that the temperature-dependent induction period (425 min/125°C, 25/165, 6/185, in which the stabiliser becomes consumed) is followed by autocatalytic and rapidly accelerating polymerisation, with Q = 0.89 kJ/g [3].

See VIOLENT POLYMERISATION

See other GLASS INCIDENTS, INDUCTION PERIOD INCIDENTS, POLYMERISATION INCIDENTS

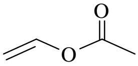
Other reactants

Yoshida, 1980, 10

MRH values calculated for 13 combinations with oxidants are given.

†1527. Vinyl acetate (Ethenyl ethanoate)

[108-05-4] **$C_4H_6O_2$**



(*MCA SD-75*, 1970); *FPA H36*, 1975; *HCS 1980*, 955

1. Harmon, 1974, 2.19
2. Levy, L. B., *Process Safety Progress*, 1993, **12**(1), 47
3. Gustin, J. L. *et al., Chem. Abs.*, 1998, **129**, 264630g

The monomer is volatile and tends to self-polymerise, and is therefore stored and handled cool and inhibited, with storage limited to below 6 months. Several industrial explosions have been recorded [1]. Unlike acrylic monomers, oxygen is not involved in stabilisation and is detrimental at higher temperatures [2]. The polymerisation has been modelled and causes of accidents proposed [3].

Air, Water

MCA SD-75, 1970

Vinyl acetate is normally inhibited with hydroquinone to prevent polymerisation. A combination of too low a level of inhibitor and warm, moist storage conditions may lead to spontaneous polymerisation. This process involves autoxidation of acetaldehyde (a normal impurity produced by hydrolysis of the monomer) to a peroxide which initiates exothermic polymerisation as it decomposes. In bulk, this may accelerate to a dangerous extent. Other peroxides or radical sources will initiate the exothermic polymerisation.

Desiccants

MCA SD-75, 1970

Vinyl acetate vapour may react vigorously in contact with silica gel or alumina.

Dibenzoyl peroxide, Ethyl acetate

Vervalin, 1973, 81

Polymerisation of the ester with dibenzoyl peroxide in ethyl acetate accelerated out of control and led to discharge of a large volume of vapour which ignited and exploded.

See other POLYMERISATION INCIDENTS

Ethylene

See Ethylene: Vinyl acetate

Hydrogen peroxide MRH 6.19/78

See Hydrogen peroxide: Vinyl acetate

Other reactants

Yoshida, 1980, 122

MRH values calculated for 15 combinations with oxidants are given.

Oxygen

Barnes, C. E. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 210

The unstabilised polymer exposed to oxygen at 50°C generated an ester—oxygen interpolymeric peroxide which, when isolated, exploded vigorously on gentle heating.

See other POLYPEROXIDES

Ozone

See Vinyl acetate ozonide

Toluene

MCA Case History No. 2087

The initial exotherm of a solution polymerisation of the ester in boiling toluene in a 10 m^3 reactor was too great for the cooling and vent systems, and the reaction began to accelerate out of control. Failure of a gasket released a quantity of the flammable reaction mixture which became ignited and destroyed the containing building.

See other PEROXIDISABLE COMPOUNDS, POLYMERISATION INCIDENTS

1528. Poly(1,3-butadiene peroxide)

[28655-95-0] **$(C_4H_6O_2)_n$**

[1225]

Butadiene

1. Alexander, D. S., *Ind. Eng. Chem.*, 1959, **51**, 733
2. Hendry, D. G. *et al., Ind. Eng. Chem., Prod. Res. Dev.*, 1968, **7**, 136, 145
3. *ASTM D1022-76*
4. Bailey, H. C., private comm., 1974

5. *CISHC Chem. Safety Summ.*, 1980, **51**, 39
6. *Sichere Chemiearb.*, 1980, **32**, 6—8
7. *MCA Case History No. 2270*

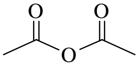
A violent explosion in a partially full butadiene storage sphere was traced to butadiene peroxide. The latter had been formed by contact with air over a long period, and had eventually initiated the exothermic polymerisation of the sphere contents. A tank monitoring and purging system was introduced to prevent a recurrence [1]. The polyperoxide (formed even at 0°C) is a mixed 1,2- and 1,4-addition copolymer of butadiene with oxygen [2], effectively a dialkyl peroxide. Its concentration in butadiene is very seriously underestimated by a standard method applicable to hydroperoxides [3], which indicates only 5% of the true value. Alternative methods of greater reliability are likely to form the basis of a revised standard method currently under consideration [4]. A bolt falling into an 'empty' rail tanker during maintenance work led to a serious explosion. Other rail tankers used to convey unstabilised butadiene were later found to contain several kg of the gelatinous polyperoxide [5]. Peroxide formation in uninhibited monomer is very rapid, air-saturated monomer giving in 24 h 124 ppm of peroxide/18°C and 460 ppm/50°C. The peroxide ($n = 7$—9) has very low solubility in the monomer, and separates as a lower layer which is very shock-sensitive and powerfully explosive [6]. Solidified peroxide plugging a tube condenser decomposed explosively during drilling operations to clear the tubes [7].

See 1,3-Butadiene

See other POLYPEROXIDES

1529. Acetic anhydride

[108-24-7] **$C_4H_6O_3$**



(*MCA SD-15*, 1962); *HCS 1980*, 101

The principal reaction hazard attached to use of acetic anhydride is the possibility of rapid and exothermic acid-catalysed hydrolysis unless the conditions prevailing (temperature, agitation, order of mixing, proportion of water) are such as to promote smooth and progressive hydrolysis with adequate heat removal. The examples below illustrate these factors.

Acetic acid, Water

MCA Case History No. 1865

Erroneous addition of aqueous acetic acid into a tank of the anhydride caused violent exothermic hydrolysis of the latter.

See Water, below

Ammonium nitrate, Hexamethylenetetraminium acetate, Nitric acid

See Nitric acid: Acetic anhydride, etc.

Barium peroxide

See Barium peroxide: Acetic anhydride

Boric acid

1. Lerner, L. M., *Chem. Eng. News*, 1973, **51**(34), 42
2. *Experiments in Organic Chemistry*, 281, Fieser, L. F., Boston, Heath, 1955

Attempted preparation of acetyl borate by slowly heating a stirred mixture of the anhydride and solid acid led to an eruptive explosion at 60°C [1]. The republished procedure being used [2] omitted the reference to a violent reaction mentioned in the German original. Modifying the procedure by adding portions of boric acid to the hot stirred anhydride should give a smoother reaction.

Bromohydroxybiphenyl, Pyridine, Water

Nolan, 1983, Case History 36

Bromohydroxybiphenyl was *O*-acetylated with excess acetic anhydride in pyridine. The excess anhydride was to be hydrolysed by addition of water, but this was done without proper control using a hosepipe. The hydrolysis reaction ran away, causing boiling and evaporation of the reactor contents.

See Acetic acid, above; Water, below

N-tert-Butylphthalamic acid, Tetrafluoroboric acid

Boyd, G. V. *et al., J. Chem. Soc., Perkin Trans. 1*, 1978, 1346

Interaction to give *N-tert*-butylphthalisoimidium tetrafluoroborate was very violent, possibly because of exothermic hydrolysis of the anhydride by the 40% aqueous tetrafluoroboric acid.

See Tetrafluoroboric acid, below

Chromic acid

1. Dawkins, A. E., *Chem. & Ind.*, 1956, 196
2. Baker, W., *Chem. & Ind.*, 1956, 280

Addition of acetic anhydride to a solution of chromium trioxide in water caused violent boiling [1], due to the acid-catalysed exothermic hydrolysis of the anhydride [2].

Chromium trioxide MRH 2.38/84

See Chromium trioxide: Acetic anhydride

1,3-Diphenyltriazene

See 1,3-Diphenyltriazene: Acetic anhydride

Ethanol, Sodium hydrogen sulfate

Staudinger, H., *Angew. Chem.*, 1922, **35**, 657

Accidental presence of the acid salt vigorously catalysed a large scale preparation of ethyl acetate, causing violent boiling and emission of vapour which became ignited and exploded.

See other CATALYTIC IMPURITY INCIDENTS

Glycerol, Phosphoryl chloride

Bellis, M. P., *Hexagon Alpha Chi Sigma* (Indianapolis), 1949, **40**(10), 40

Violent acylation occurs in catalytic presence of phosphoryl chloride, because the high viscosity of the mixture in absence of solvent prevents mixing and dissipation of the high heat of reaction.

Hydrochloric acid, Water

1. Vogel, 1957, 572—573
2. Batchelor, J. F., private comm., 1976

Crude dimethylaniline was being freed of impurities by treatment with acetic anhydride according to a published procedure [1]. However, three times the recommended proportion of anhydride was used, and the reaction mixture was ice cooled before addition of diluted hydrochloric acid to hydrolyse the excess anhydride. Hydrolysis then proceeded with explosive violence.

Hydrogen peroxide MRH 5.52/71

See Hydrogen peroxide: Acetic anhydride

Hypochlorous acid

See Hypochlorous acid: Acetic anhydride

Metal nitrates

1. Davey, W. *et al., Chem. & Ind.*, 1948, 814
2. Collman, J. P. *et al., Inorg. Synth.*, 1963, **7**, 205—207
3. James, B. D., *J. Chem. Educ.*, 1974, **51**(9), 568

Use of mixtures of metal nitrates with acetic anhydride as a nitrating agent may be hazardous, depending on the proportions of reactants and on the cation; copper nitrate or sodium nitrate usually cause violent reactions [1]. An improved procedure for the use of the anhydride—copper(II) nitration mixture [2] has been further modified [3] to improve safety aspects.

Nitric acid MRH 4.93/66

See Nitric acid: Acetic anhydride

Other reactants

Yoshida, 1980, 356

MRH values calculated for 16 combinations with oxidants are given.

Perchloric acid, Water

1. Anon., *ABCM Quart. Safety Summ.*, 1954, **25**, 3
2. Turner, H. S. *et al., Chem. & Ind.*, 1965, 1933
3. McG. Tegart, W. J., *The Electrolytic and Chemical Polishing of Metals in Research and Industry*, London, Pergamon, 2nd Ed., 1959

Anhydrous solutions of perchloric acid in acetic acid are prepared by using acetic anhydride to remove the diluting water from 72% perchloric acid. It is essential that the anhydride is added slowly to the aqueous perchloric—acetic acid mixture under conditions where it will react readily with the water, i.e. at about 10°C. Use of anhydride cooled in a freezing mixture caused delayed and violent boiling to occur. Full directions for the preparation are given [1]. A violent explosion occurred during the preparation of an electropolishing solution by addition of perchloric acid solution to a mixture of water and acetic anhydride. The cause of the explosion, the vigorously exothermic acid-catalysed hydrolysis of acetic anhydride, is avoided if water is added last to the mixture produced by adding perchloric acid solution to acetic anhydride [2]. The published directions [3] are erroneous and insufficiently detailed for safe working.

See Perchloric acid: Acetic anhydride, or: Dehydrating agents

Peroxyacetic acid

See Peroxyacetic acid: Acetic anhydride

Polyphosphoric acid, Water

Montfort, B. *et al., Bull. Soc. Chim. Fr.*, 1987, 848—854

2-Aryloxy-1,2-diarylethanones can be cyclodehydrated to diarylbenzofurans by heating with sodium acetate and acetic anhydride in polyphosphoric acid. Quenching the hot reaction mixture with water leads to initially violent acid-catalysed hydrolysis of the excess anhydride.

Potassium permanganate MRH 2.55/86

See Potassium permanganate: Acetic acid, etc.

Sodium percarbonate

See Sodium carbonate hydrogen peroxidate: Acetic anhydride

Tetrafluoroboric acid

1. Lichtenberg, D. W. *et al., J. Organomet. Chem.*, 1975, **94**, 319
2. Wudl, F. *et al., Inorg. Synth.*, 1979, **19**, 29

Dehydration of the aqueous 48% acid by addition to the anhydride is rather exothermic, and caution is advised [1]. Operation at 0°C led to an explosion [2].

See Chromic acid, above

See also Hydrochloric acid, above

See also Perchloric acid, above

4-Toluenesulfonic acid, Water

1. Jones, B. J. *et al., Clin. Chem.*, 1955, **1**, 305
2. Pearson, S. *et al., Anal. Chem.*, 1953, **25**, 813—814

Caution is advised [1] to prevent explosions when using an analytical method involving sequential addition of acetic acid, aqueous 4-toluenesulfonic acid and acetic anhydride to serum [2]. It is difficult to see why this should happen, unless the anhydride were all added before the sulfonic acid solution.

See Water, below

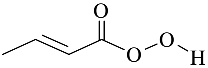
Water

1. Leigh, W. R. D. *et al., Chem. & Ind.*, 1962, 778
2. Benson, G., *Chem. Eng. News*, 1947, **25**, 3458

Accidental slow addition of water to a mixture of the anhydride and acetic acid (85:15) led to a violent, large scale explosion. This was simulated closely in the laboratory, again in the absence of mineral-acid catalyst [1]. If unmoderated, the rate of acid-catalysed hydrolysis of (water insoluble) acetic anhydride can accelerate to explosive boiling [2]. Essentially the same accident, fortunately with no injuries or fatalities this time, was repeated in 1990.

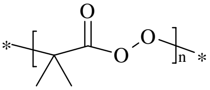
See other ACID ANHYDRIDES

1530. Peroxycrotonic acid (Peroxy-2-butenoic acid)
[5813-77-4] **$C_4H_6O_3$**



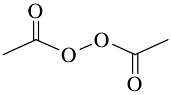
Vasilina, T. U. *et al., Chem. Abs.*, 1974, **81**, 151446
The decomposition of the acid has been mentioned in a safety context, but the details were not translated.
See other PEROXYACIDS

1531. Poly(peroxyisobutyrolactone) (Poly(dimethylketene peroxide))
[67772-28-5] **$(C_4H_6O_3)_n$**



Turro, N. J. *et al., J. Amer. Chem. Soc.*, 1978, **100**, 5580
Autoxidation of dimethylketene with oxygen in ether at —20°C gives the poly(peroxylactone) which as a dry solid is liable to undergo unpredictable and violent detonation.
See Dimethylketene
See other POLYPEROXIDES
See related PEROXYESTERS

1532. Diacetyl peroxide
[110-22-5] **$C_4H_6O_4$**



1. Shanley, E. S., *Chem. Eng. News*, 1949, **27**, 175
2. Kuhn, L. P., *Chem. Eng. News*, 1948, **26**, 3197
3. Kharasch, M. S. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 1269
4. Moore, C. G., *J. Chem. Soc.*, 1951, 236

Acetyl peroxide may readily be prepared and used in ethereal solution. It is essential to prevent separation of the crystalline peroxide even in traces, since, when dry, it is shock-sensitive and a high explosion risk [1]. Crystalline material, separated and dried deliberately, detonated violently [2]. The commercial material, supplied as a 30% solution in dimethyl phthalate, is free of the tendency to crystallise and is relatively safe. It is, however, a powerful oxidant [1]. Precautions necessary for the preparation and thermolysis of the peroxide have been detailed [3,4].
See Fluorine: Sodium acetate

Other reactants

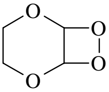
Yoshida, 1980, 134

MRH values calculated for 15 combinations with oxidisable elements and compounds are given.

See other DIACYL PEROXIDES

1533. *cis*-1,4-Dioxenedioxetane (2,5,7,8-Tetraoxa[4.2.0]bicyclooctane)

[59261-17-5] **$C_4H_6O_4$**



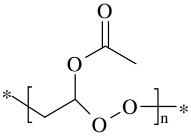
Wilson, T. *et al., J. Amer. Chem. Soc.*, 1976, **98**, 1087

A small sample of the solid peroxide exploded on warming to ambient temperature. Storage at —20°C in solution appears safe.

See other CYCLIC PEROXIDES

1534. Poly(vinyl acetate peroxide)

[ ] **$(C_4H_6O_4)_n$**

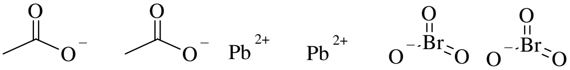


See Vinyl acetate: Oxygen

See other POLYPEROXIDES

1535. Lead acetate—lead bromate

[ ] **$C_4H_6O_4Pb.Br_2O_6Pb$**

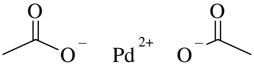


1. Berger, A., *Arbeits-Schutz.*, 1934, **2**, 20
2. Leymann, —, *Chem. Fabrik*, 1929, 360—361

The compound (formulated as the double salt, (fuel + oxidant), rather than the mixed salt) may be formed during the preparation of lead bromate from lead acetate and potassium bromate in acetic acid, and is explosive and very sensitive to friction. Although lead bromate is stable up to 180°C, it is an explosive salt [1]. Further details of the incident are available [2].

See related METAL OXOHALOGENATES

1536. Palladium(II) acetate
[3375-31-3] **$C_4H_6O_4Pd$**

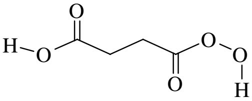


Phenylacetylene

See Phenylacetylene: Palladium(II) acetate

See related PLATINUM COMPOUNDS

1537. Monoperoxysuccinic acid
[3504-13-0] **$C_4H_6O_5$**

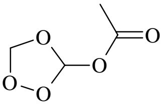


1. Lombard, R. *et al., Bull. Soc. Chim. Fr.*, 1963, **12**, 2800
2. Castrantas, 1965, 16

It explodes in contact with flame [1] and is weakly shock-sensitive [2].

See other PEROXYACIDS

1538. Vinyl acetate ozonide (3-Acetoxy-1,2,4-trioxolane)
[101672-23-5] **$C_4H_6O_5$**

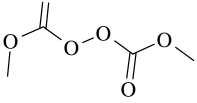


Kirk-Othmer, 1970, Vol. 21, 320

The ozonide formed by vinyl acetate is explosive when dry.

See other OZONIDES

1539. Dimethyl peroxydicarbonate
[15411-45-7] **$C_4H_6O_6$**

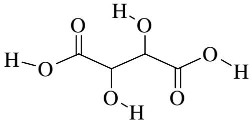


Explodes on heating to 55—60°C, or readily under a hammer blow, and more powerfully than dibenzoyl peroxide.

See entry PEROXYCARBONATE ESTERS

1540. Tartaric acid (2,3-Dihydroxybutanedioic acid)

[87-69-4] **$C_4H_6O_6$**



HCS 1980, 883

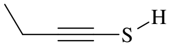
Silver

See Silver: Carboxylic acids

See other ORGANIC ACIDS

1541. 2-Butyne-1-thiol

[101672-05-3] **C_4H_6S**



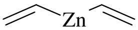
Brandsma, 1971, 180

Presence of a stabiliser is essential during handling or storage at —20°C under nitrogen. Exposure to air leads to formation of a polymer which may explode on heating.

See other ACETYLENIC COMPOUNDS

1542. Divinylzinc

[1119-22-8] **C_4H_6Zn**



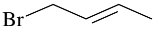
491M, 1975, 164

It ignites in air.

See related ALKYLMETALS

†1543. 1-Bromo-2-butene

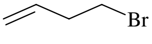
[4784-77-4] **C_4H_7Br**



See other ALLYL COMPOUNDS, HALOALKENES

†1544. 4-Bromo-1-butene

[5162-44-7] **C_4H_7Br**



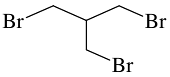
Chloromethylphenylsilane, Chloroplatinic acid

See Chloromethylphenylsilane: 4-Bromobutene, etc.

See other HALOALKENES

1545. 1,1,1-Tris(bromomethyl)methane (3-(Bromomethyl)-1,3-dibromopropane)

[62127-48-4] **$C_4H_7Br_3$**

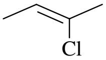


Preparative hazard

See Phosphorus tribromide: 1,1,1-Tris(hydroxymethyl)methane

†1546. 2-Chloro-2-butene

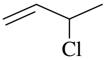
[4461-41-0] **C_4H_7Cl**



See other HALOALKENES

†1547. 3-Chloro-1-butene

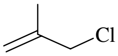
[563-52-0] **C_4H_7Cl**



See other HALOALKENES

†1548. 3-Chloro-2-methyl-1-propene

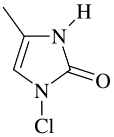
[563-47-3] **C_4H_7Cl**



See other HALOALKENES

1549. *N*-Chloro-4-methyl-2-imidazolinone

[55341-15-6] **$C_4H_7ClN_2O$**

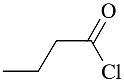


Walles, W. E., US Pat. 3 850 920, 1974

It exploded after several hours at ambient temperature.

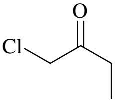
See other *N*-HALOGEN COMPOUNDS

†1550. Butyryl chloride (Butanoyl chloride)
[141-75-3] **C_4H_7ClO**



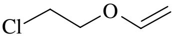
See other ACYL HALIDES

1551. 1-Chloro-2-butanone
[616-27-3] **C_4H_7ClO**



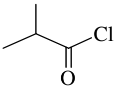
Tilford., C. H. private comm., 1965
An amber bottle of stabilised material spontaneously exploded.
See Chloroacetone

†1552. 2-Chloroethyl vinyl ether (2-Chloroethoxyethene)
[110-75-8] **C_4H_7ClO**



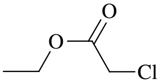
See other PEROXIDISABLE COMPOUNDS

†1553. Isobutyryl chloride (2-Methylpropanoyl chloride)
[79-30-1] **C_4H_7ClO**



See other ACYL HALIDES

1554. Ethyl chloroacetate
[105-39-5] **$C_4H_7ClO_2$**



HCS 1980, 475

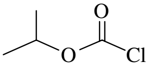
Sodium cyanide

Brown, E. A. B., private comm., 1982

A well-established procedure (1 g mol, 20 runs) for preparation of ethyl cyanoacetate by heating the reactants together suddenly erupted out of control.

†1555. Isopropyl chloroformate

[108-23-6] **$C_4H_7ClO_2$**



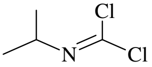
1. *491M*, 1975, 223
2. Young, J. A., *Chem. Health Saf.*, 1998, **5**(5), 4

A sample exploded in refrigerated storage. It is known that if iron salts are present during the preparation from 2-propanol and phosgene, catalysed thermal decompositon may occur [1]. A 2 litre glass bottle, presumably less than a year old and stored unrefrigerated at eye-level, exploded during stocktaking, splashing the eyes and face of a researcher [2]. Iron is usually present in glass, especially brown glass, while most eye protection is designed primarily to stop fast particles and shields poorly against slow liquids.

See other ACYL HALIDES, CATALYTIC IMPURITY INCIDENTS

1556. Isopropylisocyanide dichloride

[29119-58-2] **$C_4H_7Cl_2N$**



Iron(III) chloride, Metal oxides, or Water

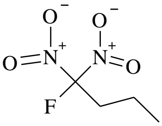
Fuks, R. *et al., Tetrahedron*, 1973, **29**, 297—298

Interaction of the 3:2 complex with iron(III) chloride and calcium oxide, mercury oxide or silver oxide was usually too violent for preparative purposes, but zinc oxide was satisfactory. Reaction with water was violent.

See related CYANO COMPOUNDS

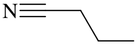
1557. 1-Fluoro-1,1-dinitrobutane

[19273-47-3] **$C_4H_7FN_2O_4$**



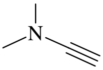
See entry FLUORODINITROMETHYL COMPOUNDS

†1558. Butyronitrile (Butanonitrile)
[109-74-0] **C_4H_7N**



See other CYANO COMPOUNDS

1559. (Dimethylamino)acetylene (*N,N*-Dimethylethynamine)
[24869-88-3] **C_4H_7N**



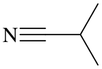
Water

Brandsma, 1971, 139

The amine reacts extremely vigorously with neutral water.

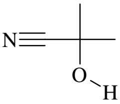
See other ACETYLENIC COMPOUNDS, ORGANIC BASES

†1560. Isobutyronitrile (2-Methylpropanonitrile)
[78-82-0] **C_4H_7N**



See other CYANO COMPOUNDS

1561. 2-Cyano-2-propanol
[75-86-5] **C_4H_7NO**



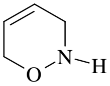
HCS 1980, 103

Sulfuric acid

See Sulfuric acid: 2-Cyano-2-propanol

See other CYANO COMPOUNDS

1562. 3,6-Dihydro-1,2,2*H*-oxazine
[3686-43-9] **C_4H_7NO**



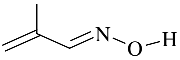
Nitric acid

See Nitric Acid: 3,6-Dihydro-1,2,2*H*-oxazine

See other N—O COMPOUNDS

1563. 2-Methylacryaldehyde oxime

[28051-68-5] **C_4H_7NO**



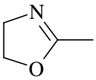
Mowry, D. T. *et al., J. Amer. Chem. Soc.*, 1947, **69**, 1831

The viscous distillation residue may decompose explosively if overheated. A polymeric peroxide may have been involved.

See other OXIMES, POLYPEROXIDES

†1564. 2-Methyl-2-oxazoline

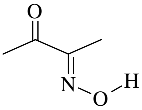
[1120-64-5] **C_4H_7NO**



See other N—O COMPOUNDS

1565. 2,3-Butanedione monoxime

[57-71-6] **$C_4H_7NO_2$**



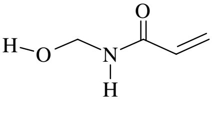
Muir, G. D., private comm., 1968

Distillation from a mantle heated flask at 6.5 mbar caused explosions on several occasions. Distillation from a steam heated flask at below 1.3 mbar appeared safe.

See other OXIMES

1566. *N*-Hydroxymethylacrylamide (*N*-Hydroxymethyl-2-propenamide)

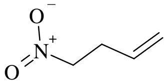
[924-42-5] **$C_4H_7NO_2$**



491M, 1975, 213

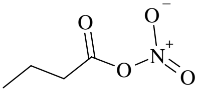
Excessive heat, smoke, flames and crackling noises were emitted from stored fibre drums of the monomer, some unopened. Polymerisation may have been initiated by minor contaminants (perhaps as vapours), and/or by excessively warm storage conditions.
See other POLYMERISATION INCIDENTS

1567. 4-Nitro-1-butene
[32349-29-4] **$C_4H_7NO_2$**



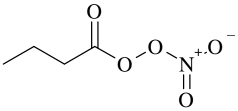
Witucki, E. F. *et al., J. Org. Chem.*, 1972, **37**, 152
A fume-off during distillation of one sample of this compound (b.p., 55°C/25 mbar) illustrates the inherent instability of this type of compound.

1568. Butyryl nitrate
[101672-06-4] **$C_4H_7NO_4$**



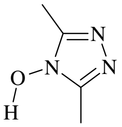
Francis, F. E., *Ber.*, 1906, **39**, 3798
It detonates on heating.
See other ACYL NITRATES

1569. Butyryl peroxonitrate
[5796-89-4] **$C_4H_7NO_5$**



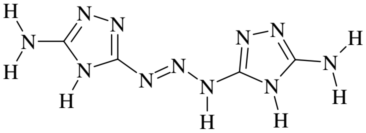
Stephens, E. R., *Anal. Chem.*, 1964, **36**, 928
It is highly explosive, like its lower homologues.
See related PEROXYESTERS

1570. 4-Hydroxy-3,5-dimethyl-1,2,4-triazole
[35869-74-0] **$C_4H_7N_3O$**



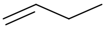
Armand, J. *et al., J. Chem. Res. (M)*, 1980, 3868
It explodes on melting at 122°C.
See other N—O COMPOUNDS, TRIAZOLES

1571. 1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene
[3751-44-8] **$C_4H_7N_{11}$**



Hauser, M., *J. Org. Chem.*, 1964, **29**, 3449
It explodes at the m.p., 187°C.
See other HIGH-NITROGEN COMPOUNDS, TRIAZOLES

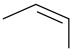
†1572. 1-Butene
[106-98-9] **C_4H_8**



HCS 1980, 229 (cylinder)

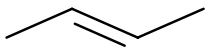
Aluminium tetrahydroborate
See Aluminium tetrahydroborate: Alkenes, etc.
See other ALKENES

†1573. *cis*-2-Butene
[624-64-6] **C_4H_8**



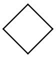
See other ALKENES

†1574. *trans*-2-Butene
[590-18-1] **C_4H_8**

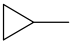


See other ALKENES

†1575. Cyclobutane
[287-23-0] **C_4H_8**

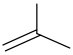


†1576. Methylcyclopropane
[594-11-6] **C_4H_8**



See other STRAINED-RING COMPOUNDS

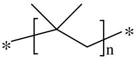
†1577. 2-Methylpropene (Isobutene)
[115-11-7] **C_4H_8**



FPA H108, 1981; *HCS 1980*, 566

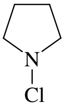
See other ALKENES

1578. Poly(isobutene)
[9003-27-4] **$(C_4H_8)_n$**



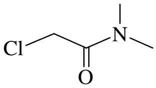
Silver peroxide
See Silver peroxide: Poly(isobutene)

1579. *N*-Chloropyrrolidine
[19733-68-7] **C_4H_8ClN**



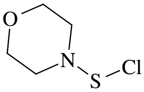
It explodes at ambient temperature.
See entry *N*-HALOGEN COMPOUNDS (reference 4)

1580. *N,N*-Dimethyl-2-chloroacetamide
[2675-89-0] **C_4H_8ClNO**



Energy of decomposition (in range 180—440°C) measured as 0.59 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

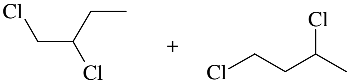
1581. 4-Morpholinesulfenyl chloride
[2958-89-6] **C_4H_8ClNOS**



MCA Case History No. 1806

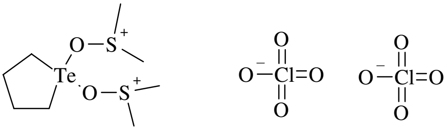
The product from chlorination of 4,4′-dithiodimorpholine exploded violently after vacuum stripping of the solvent carbon tetrachloride. As it was a published process that previously had been operated uneventfully, no cause was apparent. It seems remotely possible that an unstable *N*-chloro derivative could have been produced by N—S bond cleavage if chlorination conditions had differed from those previously employed.
See other *N*—S COMPOUNDS

†1582. *mixo*-Dichlorobutane
[26761-81-9] **$C_4H_8Cl_2$**



See other HALOALKANES

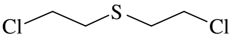
1583. 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate
[100242-83-9] **$C_4H_8Cl_2O_8.2C_2H_6OS$**



Srivastava, T. *et al.*, *Polyhedron*, 1985, **4**, 1223—1229
The complex explodes at its m.p., 116°C.
See other ORGANOMETALLIC PERCHLORATES

1584. Bis(2-chloroethyl)sulfide (1,1′-Thiobis(2-chloroethane))

[505-60-2] **$C_4H_8Cl_2S$**

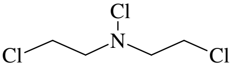


Bleaching powder

See BLEACHING POWDER

1585. *N*-Chloro-bis(2-chloroethyl)amine

[63915-60-6] **$C_4H_8Cl_3N$**



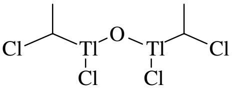
Butters, M. *et al.*, UK Pat. Appl. GB 2 165 244, 1986

The *N*-chloro derivative is potentially explosive when neat, often exploding during distillation at 60°C/2.6 mbar.

See other *N*-HALOGEN COMPOUNDS

1586. Bis(1-chloroethylthallium chloride) oxide

[ ] **$C_4H_8Cl_4OTl_2$**



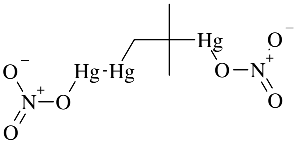
Yakubovich, A. Ya. *et al., Doklad. Akad. Nauk SSSR*, 1950, **73**, 957—958

An explosive solid of low stability.

See related ALKYLMETALS, METAL HALIDES, METAL OXIDES

1587. 2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane

[ ] **$C_4H_8Hg_3N_2O_6$**



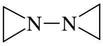
Whitmore, 1921, 116

The compound, prepared from isobutene and mercury(II) nitrate, explodes on impact at 80°C.

See other ORGANOMETALLIC NITRATES

1588. 1,1′-Biaziridinyl

[4388-03-8] **$C_4H_8N_2$**



Oxygen

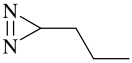
Graefe, A. F., *J. Amer. Chem. Soc.*, 1958, **80**, 3941

It exploded violently during analytical combustion in oxygen.

See other AZIRIDINES

1589a. 3-Propyldiazirine

[70348-66-2] **$C_4H_8N_2$**



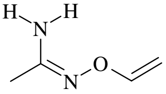
Schmitz, E. *et al., Ber.*, 1962, **95**, 800

It exploded on attempted distillation from calcium chloride at about 75°C.

See other DIAZIRINES

1589b. *N*-Ethenyloxyethanimidamide (*N*-Vinyloxyacetamidine)

[263699-23-6] **$C_4H_8N_2O$**



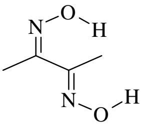
Trofimov, B. A. *et al., Synthesis*, 2001, (16), 2427

It is reported as decomposing violently at around 150°C.

See other N—O COMPOUNDS

1590. Butane-2,3-dione dioxime

[95-45-4] **$C_4H_8N_2O_2$**



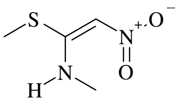
Energy of decomposition (in range 220—360°C) measured as 1.98 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other OXIMES

1591. 1-Methylamino-1-methylthio-2-nitroethene (*N*-Methyl-1-(methylthio)-2-nitroethenamine)

[61832-41-5] **$C_4H_8N_2O_2S$**



Preparative hazard

1. Koshy, A. *et al., J. Hazard. Mater.*, 1995, 42(3), 215
2. Goulding, J. P. in *Safety and Runaway Reactions*, Smeder, B & Mitchison, N. (Eds.), EUR 17723 EN, European Commission, 1997, p31

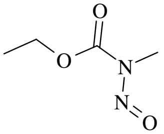
This pharmaceutical intermediate, itself unstable, is prepared via intermediates which are actually explosive. A calorimetric study of risks is reported [1]. The byproducts are also hazardous, a study into an explosion and fire consequent upon isopropanol (solvent) recovery from a manufacturing process is reported [2]. This was done by distillation, leaving a concentrated residue, more than one distillation being performed before the residue was discharged for incineration. A fortnight's accumulated residue, as about a 25% solution or suspension in isopropanol was left in the reactor for a week. This was probably below minimum stir volume and below the level of the temperature probe. During this week, there was a power cut which appears to have stopped the flow of coolant to the reactor; the coolant coils may in any event not have dipped far into the residue. Two days later, shortly preceded by some indications of modest warming, the explosion occurred, rupturing storage tanks, igniting their contents and thus causing considerable secondary damage. Calorimetry suggested that the deposited solids became unsafe at 40°C, the stirred bulk from about 65°C. It was concluded that both the design and operation of the recovery process had been inadequate [2]. (Elsewhere in this book, an account of another explosion and destructive sequence of secondary fires, when treating wastes from a slightly different manufacturing process, is to be found. In this other case neither product nor byproducts were directly responsible – Ed.)

See Nitromethane; Carbon disulfide

See other *C*-NITRO COMPOUNDS

1592. Ethyl *N*-methyl-*N*-nitrosocarbamate

[615-53-2] **$C_4H_8N_2O_3$**

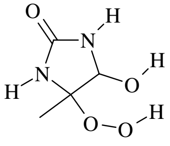


1. Hartman, W. W., *Org. Synth.*, 1943, Coll. Vol. 2, 465
2. Druckrey, H. *et al., Nature*, 1962, **195**, 1111

The material is unstable and explodes if distilled at ambient pressure [1], or may become explosive if stored above 15°C [2]. Its use for preparation of diazomethane has been superseded by more stable intermediates.

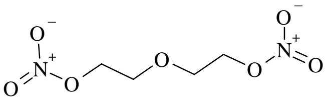
See Diazomethane
See other NITROSO COMPOUNDS

1593. *trans*-4-Hydroperoxy-5-hydroxy-4-methylimidazolin-2-one
[85576-52-9] **$C_4H_8N_2O_4$**



Preparative hazard
See Hydrogen peroxide: 2-Amino-4-methyloxazole
See related ALKYL HYDROPEROXIDES

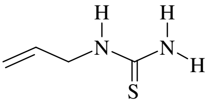
1594. 2,2′-Oxybis(ethyl nitrate)
[693-21-0] **$C_4H_8N_2O_7$**



1. Kit and Evered, 1960, 268
2. Toso, R. *et al., Chem. Abs.*, 1988, **108**, 24140

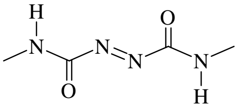
A powerful explosive, sensitive to vibration and mechanical shock, too heat-sensitive for a rocket propellant [1]. In the industrial preparation of this explosive by the continuous nitration of diethylene glycol by nitric—sulfuric acid mixtures, the main factor limiting the overall safety of the process is the instability of the spent acid mixture, and handling of the latter is the most important specific problem. Close control of the acid composition and of the glycol:acid ratio reduces the nitric acid and water contents of the organic phase in the reaction mixture, and so increases the stability of the organic phase. Continuous addition of oleum to the spent acid coming from the separator increases its stability and permits safe handling and storage [2].
See other ALKYL NITRATES, NITRATION INCIDENTS

1595. *N*-Allylthiourea
[109-57-9] **$C_4H_8N_2S$**



Energy of decomposition (in range 170—270°C) measured as 0.549 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ALLYL COMPOUNDS

1596. Azo-*N*-methylformamide
[18880-14-3] $C_4H_8N_4O_2$

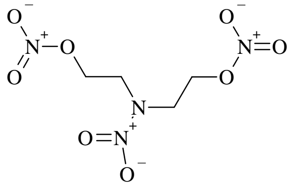


Smith, R. F. *et al., J. Org. Chem.*, 1975, **40**, 1855

Thermolysis is vigorously exothermic, the temperature increasing from 176 to 259°C during decomposition.

See other AZO COMPOUNDS, BLOWING AGENTS

1597. Bis(2-nitratoethyl)nitric amide
[4185-47-1] $C_4H_8N_4O_8$



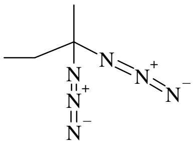
Chromium compounds

Aleksandrov, V. V. *et al., Combust. Flame*, 1979, **35**, 1—15

The burning rate of the solid explosive is increased by various chromium compounds.

See related ALKYL NITRATES, N—NITRO COMPOUNDS

1598. 2,2-Diazidobutane
[90329-44-5] $C_4H_8N_6$

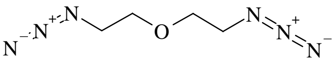


Kirchmeyer, S. *et al., Synthesis*, 1983, 501

Potentially explosive (a *gem*-diazide).

See other ORGANIC AZIDES

1599. 1,1′-Oxybis-2-azidoethane
[24345-74-2] $C_4H_8N_6O$



1. Rankine A., *Safety Digest Univ. Safety Assn.*, 1992, **43**, 22
2. Peacock, R. D., *Chemistry in Britain*, 1992, **28**(4), 327

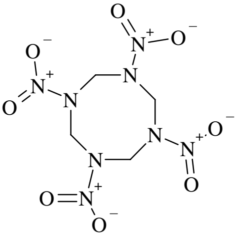
An explosion was experienced during isolation of supposed diamine produced by reduction of the diazide with hydrogen sulfide. This was attributed to incomplete reduction [1]. An explosion, apparently during reduction, of a closely related compound by this method has earlier been reported [2].

See 1,2-Bis(2-azidoethoxy)ethane

See other ORGANIC AZIDES

1600. 1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine

[2691-41-0] **$C_4H_8N_8O_8$**



1. Corignan, Y. P. *et al., J. Org. Chem.*, 1967, **32**, 285
2. Mc Crone, W. C., *Chem. Eng. News*, 1999, **77**(27), 2

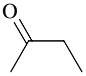
The military explosive HMX. Violent decomposition occurred at 279°C [1]. HMX has several crystalline forms, only one of which is ‘safe’;, another being as sensitive as lead azide [2].

See 1,3,5-Trinitrohexahydro-1,3,5-triazine

See other N—NITRO COMPOUNDS

†1601. 2-Butanone (Ethyl methyl ketone)

[78-93-3] **C_4H_8O**



(*MCA SD-83*, 1961); *FPA H16*, 1973; *HCS 1980*, 650; *RSC Lab. Hazard Data Sheet No. 18*, 1983

Chloroform, Alkali

See Chloroform: Acetone, etc.

Hydrogen peroxide	MRH 6.36/83
Nitric acid	MRH 5.77/79

See Hydrogen peroxide: Ketones, etc.

Other reactants

Yoshida, 1980, 365

MRH values calculated for 13 combinations with oxidants are given.

Potassium *tert*-butoxide

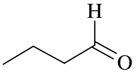
See Potassium *tert*-butoxide: Acids, etc.

2-Propanol

See 2-Propanol: 2-Butanone

†1602. Butyraldehyde (Butanal)

[123-72-8] **C_4H_8O**

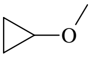


(*MCA SD-78*, 1960); *FPA H70*, 1978; *HCS 1980*, 254

See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

†1603. Cyclopropyl methyl ether (Methoxycyclopropane)

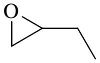
[540-47-6] **C_4H_8O**



See other PEROXIDISABLE COMPOUNDS, STRAINED-RING COMPOUNDS

†1604. 1,2-Epoxybutane (Ethyloxirane)

[106-88-7] **C_4H_8O**



HCS 1980, 455

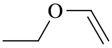
Dinitrogen pentaoxide

See Dinitrogen pentaoxide: Oxygen heterocycles

See other 1,2-EPOXIDES, STRAINED-RING COMPOUNDS

†1605. Ethyl vinyl ether (Ethoxyethene)

[109-92-2] **C_4H_8O**



Methanesulfonic acid

Eaton, P. E. *et al. J. Org. Chem.*, 1972, **37**, 1947

Methanesulfonic acid is too powerful a catalyst for *O*-alkylation with the vinyl ether, causing explosive polymerisation of the latter on multimolar scale. Dichloroacetic acid is a satisfactory catalyst on the 3 g mol scale.

Other reactants

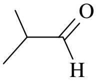
Yoshida, 1980, 288

MRH values calculated for 13 combinations with oxidants are given.

See other PEROXIDISABLE COMPOUNDS

†1606. Isobutyraldehyde (2-Methylpropanal)

[78-84-2] C_4H_8O

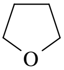


(*MCA SD-78*, 1960)

See other PEROXIDISABLE COMPOUNDS

†1607. Tetrahydrofuran

[109-99-9] C_4H_8O



FPA H60, 1977; *HCS 1980*, 891; *RSC Lab. Hazard Data Sheet No. 12*, 1983

1. *Recommended Handling Procedures*, THF Brochure FC3-664, Wilmington, Du Pont, 1964
2. Anon., *Org. Synth.*, 1966, **46**, 105
3. Schurz, J. *et al., Angew. Chem.*, 1956, **68**, 182
4. Davies, A. G., *J. R. Inst. Chem.*, 1956, **80**,386
5. Halonbrenner, R. *et al., Chem. Eng. News*, 1978, **56**(6), 3
6. Coates, J. S., *Chem. Eng. News*, 1978, **56**(6), 3
7. Wissink, H. G. , *Chem. Eng. News*, 1997, **75**(9), 6
8. Schwartz, A. M., *Chem. Eng. News*, 1978, **56**(24), 88
9. Hanson, E. S., *Chem. Eng. News*, 1978, **56**(24), 88
10. Nagano, H., *Chem. Abs.*, 1980, **92**, 163833

Like many other ethers and cyclic ethers, in absence of inhibitors tetrahydrofuran is subject to autoxidation on exposure to air, when initially the 2-hydroperoxide forms. This tends to decompose smoothly when heated, but if allowed to accumulate for a considerable period, it becomes transformed into other peroxidic species which will decompose violently [1]. Commercial material is supplied stabilised with a phenolic antioxidant which is effective under normal closed storage conditions in preventing the formation and accumulation of peroxide. Procedures for testing for the presence of peroxides and also for their removal are detailed [1,2,4]. The last of these references recommends the use of copper(I) chloride for removal of trace amounts of peroxide. If more than trace amounts are present, the peroxidised solvent (small quantities only) should be discarded by dilution and flushing away with water [2]. An attempt to remove peroxides by shaking with solid ferrous sulfate before distillation did not prevent explosion of the distillation residue [3]. Alkali treatment to destroy peroxides [1] appears not to be safe [2]. (See Caustic alkalies, below). Distillation or alkali treatment of stabilised THF removes the involatile antioxidant and the solvent must be restabilised or stored under nitrogen to prevent peroxide formation during storage, which should not exceed a few days' duration in the absence of stabiliser [2]. The use of lithium

tetrahydroaluminate is only recommended for drying THF which is peroxide-free and is not grossly wet [2]. A violent explosion during reflux of the solvent with calcium hydride [5] was attributed to cleavage of the cyclic ether by overheated excess hydride [6]. Other metal hydrides (and some other strong bases) can also cause decomposition to ethene and enolate salts of acetaldehyde [7], pressurising containers by gas emission. The use of sodium benzophenone ketyl [8], or of an activated alumina column [9] to remove moisture and peroxides are detailed. Peroxides in THF may be destroyed by passage through activated carbon at 20—66°C with contact time > 2 min [10].
See 2-Tetrahydrofuryl hydroperoxide
See also ETHERS (references [9, 10])

2-Aminophenol, Potassium dioxide
See Potassium dioxide: 2-Aminophenol, Tetrahydrofuran

Borane
See Borane—tetrahydrofuran

Bromine
See Bromine: Tetrahydrofuran

Calcium hydride
See (references [5,6])

Caustic alkalies
1. *NSC Newsletter, Chem. Sect.*, 1964(10); 1967(3)
2. Anon., *Org. Synth.*, 1966, **46**, 105

It is not safe to store quantities of THF which have been freed of the phenolic inhibitor (e.g. by alkali treatment) since dangerous quantities of peroxides may build up in prolonged storage. Peroxidised materials should not be dried with sodium hydroxide or potassium hydroxide, as explosions may occur [1,2].

Diisobutylaluminium hydride
See Diisobutylaluminium hydride: Tetrahydrofuran

Lithium tetrahydroaluminate
See Lithium tetrahydroaluminate: Tetrahydrofuran

Metal halides
See Hafnium tetrachloride: Tetrahydrofuran
Titanium tetrachloride: Tetrahydrofuran
Zirconium tetrachloride: Tetrahydrofuran

Other reactants
Yoshida, 1980, 238
MRH values calculated for 12 combinations with oxidants are given.

Oxygen, strong base
Butora, G. *et al., J. Amer. Chem. Soc.*, 1997, **119**(33), 7694
As part of a synthesis, a rather dilute THF solution of an heterocycle, converted into a dianion with sec-butyllithium, was oxidised by bubbling gaseous oxygen through at —78°C. In the light of above entries, formation of peroxides is not surprising;

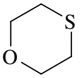
however, the reaction tended to inflame or explode while still warming to ambient temperature for treatment with deperoxidising reagents. The technique is not recommended and an electrochemical alternative, far superior both in yield and safety, was devised.

Sodium tetrahydroaluminate
See Sodium tetrahydroaluminate: Tetrahydrofuran

Sulfinyl chloride
See Sulfinyl chloride: Tetrahydrofuran
See other APROTIC SOLVENTS, PEROXIDISABLE COMPOUNDS

1608. 1,4-Oxathiane

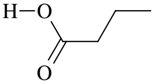
[15980-15-1] **C_4H_8OS**



Metal perchlorates
See Silver perchlorate: 1,4-Oxathiane
Copper(I) perchlorate: 1,4-Oxathiane

1609. Butyric acid (Butanoic acid)

[107-92-6] **$C_4H_8O_2$**

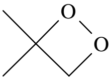


HCS 1980, 255

Chromium trioxide
See Chromium trioxide: Butyric acid
See other ORGANIC ACIDS

1610. 3,3-Dimethyl-1,2-dioxetane

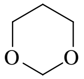
[32315-88-1] **$C_4H_8O_2$**



Adam, W. *et al., J. Amer. Chem. Soc.*, 1994, **116**(17), 7581
This molecule sometimes detonated spontaneously even below 0°C. The trimethyl and tetramethyl homologues should not be handled above 0°C and the precursor bromohydroperoxides are also hazardous.
See other CYCLIC PEROXIDES, DIOXETANES, STRAINED-RING COMPOUNDS

†1611. 1,3-Dioxane

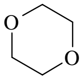
[505-22-6] **$C_4H_8O_2$**



See other PEROXIDISABLE COMPOUNDS

†1612. 1,4-Dioxane

[123-91-1] **$C_4H_8O_2$**



HCS 1980, 442; *RSC Lab. Hazard Data Sheet No. 29*, 1984

Dasler, W. *et al., Ind. Eng. Chem. (Anal. Ed.)*, 1946, **18**, 52
Like other monofunctional ethers but more so because of the four susceptible hydrogen atoms, dioxane exposed to air is susceptible to autoxidation with formation of peroxides which may be hazardous if distillation (causing concentration) is attempted. Because it is water-miscible, treatment by shaking with aqueous reducants (iron(II) sulfate, sodium sulfide, etc.) is impracticable. Peroxides may be removed, however, under anhydrous conditions by passing dioxane (or any other ether) down a column of activated alumina. The peroxides (and any water) are removed by adsorption onto the alumina, which must then be washed with methanol or water to remove them before the column material is discarded [1]. The heat of decomposition of dioxane has been determined (130—200°C) as 0.165 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Decaborane(14)
See Decaborane(14): Ether, etc.

Nickel
Mozingo, R., *Org. Synth.*, 1955, Coll. Vol. 3, 182
Dioxane reacts with Raney nickel catalyst almost explosively above 210°C.

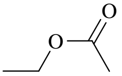
Nitric acid, Perchloric acid MRH Nitric acid 5.81/74
See Perchloric acid: Dioxane, Nitric acid

Other reactants
Yoshida, 1980, 150
MRH values calculated for 14 combinations with oxidants are given.

Sulfur trioxide MRH 2.26/38
See Sulfur trioxide: Diethyl ether, etc.

Triethynylaluminium
See Triethynylaluminium: Dioxane
See other APROTIC SOLVENTS, PEROXIDISABLE COMPOUNDS

†1613. Ethyl acetate (Ethyl ethanoate)
[141-78-6] **$C_4H_8O_2$**



(*MCA SD-51*, 1953); *FPA H8*, 1973; *HCS 1980*, 462; *RSC Lab. Hazards Data Sheet No. 41*, 1985

1. Anon., *Loss. Prev. Bull.*, 1977, (013), 16
2. Bond, J., *Loss Prev. Bull.*, 1994, (119), 9
3. Spencer, R., *Chem. Eng. Progr.*, 2003, **99**(9), 6

During rotary evaporation of solvent (from an ethyl acetate extract of a fermentation culture) at 55°C/50 mbar, the flask exploded. (It seems likely that some unsuspected peroxidised material may have been present in the extract, or perhaps the flask was scratched or cracked, and imploded [1].) Several fires and explosions suggest that ethyl acetate may be a worse generator of static electricity than its measured conductivity would indicate, and should be treated as such [2,3].

See Hydrogen peroxide: Ethyl acetate

See other STATIC INITIATION INCIDENTS

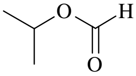
Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Ethyl acetate

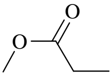
Potassium *tert*-butoxide

See Potassium *tert*-butoxide: Acids, etc.

†1614. Isopropyl formate
[625-55-8] **$C_4H_8O_2$**

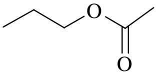


†1615. Methyl propionate
[554-12-1] **$C_4H_8O_2$**



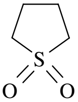
HCS 1980, 659

†1616. Propyl formate
[110-74-7] **$C_4H_8O_2$**



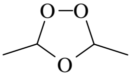
Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

1617. Tetrahydrothiophene-1,1-dioxide (Sulfolane)
[126-33-0] **$C_4H_8O_2S$**



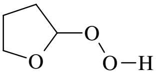
Nitronium tetrafluoroborate
See NITRATING AGENTS
See other APROTIC SOLVENTS

1618. *trans*-2-Butene ozonide (3,5-Dimethyl-1,2,4-trioxolane)
[16187-15-8] **$C_4H_8O_3$**



See trans-2-Hexene ozonide
See other OZONIDES

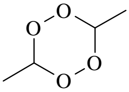
1619. 2-Tetrahydrofuryl hydroperoxide
[4676-82-8] **$C_4H_8O_3$**



1. Rein, H., *Angew. Chem.*, 1950, **62**, 120
2. Criegee, R., *Angew. Chem.*, 1950, **62**, 120

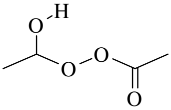
This occurs as the first product of the ready autoxidation of tetrahydrofuran, and is relatively stable [1]. It readily changes, however, to a highly explosive polyalkylidene peroxide, which is responsible for the numerous explosions observed on distillation of peroxidised tetrahydrofuran [2].
See Tetrahydrofuran
See other ALKYL HYDROPEROXIDES

1620. 3,6-Dimethyl-1,2,4,5-tetraoxane
cis [102502-32-9]; trans [118171-56-5] **$C_4H_8O_4$**



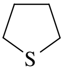
Rieche, A. *et al., Ber.*, 1939, **72**, 1933
This dimeric ‘ethylidene peroxide’ is an extremely shock-sensitive solid which explodes violently at the slightest touch. Extreme caution in handling is required.
See other CYCLIC PEROXIDES

1621. 1-Hydroxyethyl peroxyacetate
[7416-48-0] **$C_4H_8O_4$**



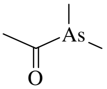
An explosive low-melting solid, readily formed during autoxidation of acetaldehyde.
See Acetaldehyde: Cobalt acetate, etc.
See other PEROXYESTERS

†1622. Tetrahydrothiophene
[110-01-0] **C_4H_8S**



Hydrogen peroxide
See Hydrogen peroxide: Tetrahydrothiophene

1623. Acetyldimethylarsine
[21380-82-5] **C_4H_9AsO**

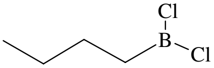


DOC 5, 1982, 38

It ignites in air.
See related ALKYLNON-METALS

1624. Butyldichloroborane

[14090-22-3] **$C_4H_9BCl_2$**



Air, or Water

Niedenzu, K. *et al., Inorg. Synth.*, 1967, **10**, 126

It ignites on prolonged exposure to air; hydrolysis may be explosive.

See other ALKYLHALOBORANES

1625. But-2-en-2-ylboronic acid

[125261-72-5] E- [125261-73-6] Z- **$C_4H_9BO_2$**

$CH_3CH{=}C(CH_3).B(OH)_2$

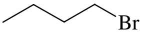
Trombini C. *et al. J. Chem. Soc. Perk. 1*, 1989, 1025

The compound is pyrophoric when dry.

See other PYROPHORIC COMPOUNDS

†1626. 1-Bromobutane (*n*-Butyl bromide)

[109-65-9] **C_4H_9Br**



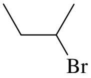
Bromobenzene, Sodium

See Sodium: Halocarbons (reference 7)

See other HALOALKANES

†1627. 2-Bromobutane (*sec*-Butyl bromide)

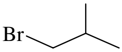
[78-76-2] **C_4H_9Br**



See other HALOALKANES

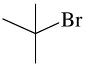
†1628. 1-Bromo-2-methylpropane (Isobutyl bromide)

[78-77-3] **C_4H_9Br**



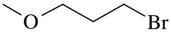
See other HALOALKANES

†1629. 2-Bromo-2-methylpropane (*tert*-Butyl bromide)
[507-19-7] **C_4H_9Br**

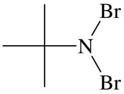


See other HALOALKANES

†1630. 2-Bromoethyl ethyl ether
[592-55-2] **C_4H_9BrO**



1631. 1,1-Dimethylethyldibromamine (*tert*-Butyldibromamine)
[51655-36-8] **$C_4H_9Br_2N$**



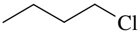
Kille, G. *et al., Ind. Chem. Libr.*, 1991, **3**(1), 75; *Chem. Abs.*, 1992, **116620(11)**, 105572

Differential scanning calorimetry (DSC) showed this to be prone to highly exothermic decomposition (100 J/g) at ambient temperatures. Solutions are a little more stable.

See also DIFFERENTIAL SCANNING CALORIMETRY

See other *N*-HALOGEN COMPOUNDS

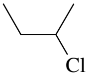
†1632. 1-Chlorobutane (*n*-Butyl chloride)
[109-69-3] **C_4H_9Cl**



HCS 1980, 297

See other HALOALKANES

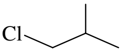
†1633. 2-Chlorobutane (*sec*-Butyl chloride)
[78-86-4] **C_4H_9Cl**



See other HALOALKANES

†1634. 1-Chloro-2-methylpropane (Isobutyl chloride)

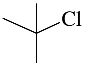
[513-36-0] **C_4H_9Cl**



See other HALOALKANES

†1635. 2-Chloro-2-methylpropane (*tert*-Butyl chloride)

[507-20-0] **C_4H_9Cl**

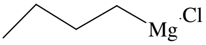


HCS 1980, 304

See other HALOALKANES

1636. Butylmagnesium chloride

[693-04-9] **C_4H_9ClMg**



Water

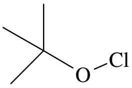
Nolan, 1983, Case history 109

Butylmagnesium chloride was prepared by adding a mixture of ether, butyl chloride and butyl bromide to magnesium, then cyclohexane was added prior to adding stannic chloride to form tetrabutyltin. However, the cyclohexane contained water and this reacted with the Grignard reagent to liberate butane which ruptured the bursting disk and ignited.

See other GAS EVOLUTION INCIDENTS, GRIGNARD REAGENTS

1637. *tert*-Butyl hypochlorite

[507-40-4] **C_4H_9ClO**



1. Lewis, J. C., *Chem. Eng. News*, 1962, **40**(43), 62
2. Teeter, H. M. *et al., Org. Synth.*, 1962, Coll. Vol. 4, 125
3. Mintz, M. J. *et al., Org. Synth.*, 1973, Coll. Vol. 5, 185

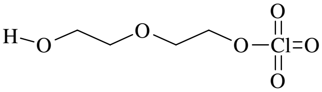
This material, normally supplied or stored in sealed ampoules and used as a paper chromatography spray reagent, is photo-sensitive. Exposure to UV light causes exothermic decomposition to acetone and chloromethane. Ampoules have burst because of pressure build-up after exposure to fluorescent or direct day light. Store

cool and dark, and open ampoules with personal protection. The material also reacts violently with rubber [1,2]. It should not be heated to above its boiling point [3]. There is also a preparative hazard.
See Chlorine: *tert*-Butanol

Sodium hydrogen cyanamide
See Cyanonitrene
See other HYPOHALITES, IRRADIATION DECOMPOSITION INCIDENTS

1638. 2(2-Hydroxyethoxy)ethyl perchlorate

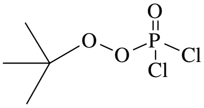
[ ] **$C_4H_9ClO_6$**



Hofmann, K. A. *et al., Ber.*, 1909, **42**, 4390
It explodes violently on heating in a capillary.
See other ALKYL PERCHLORATES

1639. *tert*-Butyl peroxophosphoryl dichloride

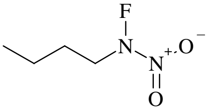
[ ] **$C_4H_9Cl_2O_3P$**



The product decomposed violently after isolation.
See entry tert-BUTYL PEROXOPHOSPHATE DERIVATIVES

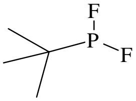
1640. *N*-Fluoro-*N*-nitrobutylamine

[14233-86-4] **$C_4H_9FN_2O_2$**



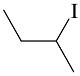
Grakauskas, V. *et al., J. Org. Chem.*, 1972, **37**, 334
A sample exploded on vacuum distillation at 60°C, though not at 40°C/33 mbar.
See other *N*-HALOGEN COMPOUNDS, N—NITRO COMPOUNDS

1641. *tert*-Butyldifluorophosphine
[29149-32-4] **$C_4H_9F_2P$**



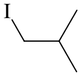
Stelzer, O. *et al., Inorg. Synth.*, 1978, **18**, 174
It ignites in air.
See other ALKYLHALOPHOSPHINES

†1642. 2-Iodobutane (*sec*-Butyl iodide)
[513-48-4] **C_4H_9I**



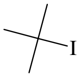
See other HALOALKANES

†1643. 1-Iodo-2-methylpropane (Isobutyl iodide)
[513-38-2] **C_4H_9I**



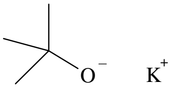
See other HALOALKANES

†1644. 2-Iodo-2-methylpropane (*tert*-Butyl iodide)
[558-17-8] **C_4H_9I**



See other HALOALKANES

1645. Potassium *tert*-butoxide
[865-47-4] **C_4H_9KO**



Fieser, 1967, Vol. 1, 911

This extremely powerful base may ignite if exposed to air (or oxygen) at elevated temperatures.
See other PYROPHORIC MATERIALS

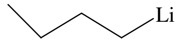
Acids, or Reactive solvents

1. Manwaring, R. *et al., Chem. & Ind.*, 1973, 172
2. Contact of 1.5 g portions of the solid butoxide with drops of the liquid (l) or with the vapours (v) of the reagents below caused ignition after the indicated period (min).
3. Acetic acid, v, 3; sulfuric acid, l, 0.5
4. Methanol, l, 2; ethanol, v, 7; propanol, l, 1; isopropanol, l, 1
5. Ethyl acetate, v, 2; butyl acetate, v, 2; propyl formate, v, 4; dimethyl carbonate, l, 1; diethyl sulfate, l, 1
6. Acetone, v, 4, l, 2; 2-butanone, v, 1, l, 0.5; 4-methyl-2-butanone, v, 3
7. Dichloromethane, l, 2; chloroform, v, 2, l, 0; carbon tetrachloride, l, 1; 1-chloro-2,3-epoxypropane, l,1

The potentially dangerous reactivity with water, acids or halocarbons was already known, but that arising from contact with alcohols, esters or ketones was unexpected. Under normal reaction conditions, little significant danger should exist where excess of solvent will dissipate the heat, but accidental spillage of the solid butoxide could be hazardous.

Dimethyl sulfoxide
See Dimethyl sulfoxide: Metal alkoxides
See other METAL ALKOXIDES

1646. Butyllithium
[109-72-8] **C_4H_9Li**



Air, or Carbon dioxide, or Water

1. (*MCA SD-91*, 1966)
2. Dezmelyk, E. W. *et al., Ind. Eng. Chem.*, 1961, **53**(6), 56A

This reactive liquid is now normally supplied commercially as a solution (up to 25 wt.%) in pentane, hexane or heptane, because it reacts with ether and ethereal solutions must be stored under refrigeration. Reaction with atmospheric oxygen or water vapour is highly exothermic and solutions of 20% concentration will ignite on exposure to air at ambient temperature and about 70% relative humidity. Solutions of above 25% concentration will ignite at any humidity. Contact with liquid water will cause immediate ignition of solutions in these highly flammable solvents [1]. Though contact with carbon dioxide causes an exothermic reaction, it is less than with atmospheric oxygen, so carbon dioxide extinguishers are effective on butyllithium fires. Full handling, operating and disposal procedures are detailed [2].

Cellulose

USA Office of Nuclear and Facility Safety, Operating Experience Weekly Summary 95-23, 1995

Butyl lithium was being used in a glove box, a spillage was cleaned up with paper towels later removed and treated with water. A towel which reached a waste bin unwetted later ignited starting a small fire [1]. (It is the editor's experience that butyl lithium solutions falling on cellulose in air ignite more often than not: destroy alkyllithiums first, mop up later.)

Sodium *tert.* butoxide, Dimethyl sulfide

Morales, D. *et al., Organometallics*, 2001, **20**(22), 4517

Even tiny quantities of the solid left after evaporation of a hexane solution of equimolar butoxide and butyl lithium, with excess sulfide, exploded violently on exposure to air.

Styrene

See Styrene: Butyllithium

Styrene

See Styrene: Butyllithium

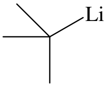
Water

See Air, etc., above

See other ALKYLMETALS

1647. *tert*-Butyllithium

[594-19-4] **C_4H_9Li**



Turbitt, T. D. *et al., J. Chem. Soc., Perkin Trans. 2*, 1974, 183

The 2M solution in heptane ignites in air.

Copper(I) iodide, Tetrahydrofuran

Kurzen, H. *et al., J. Org. Chem.*, 1985, **50**, 3222

t-Butyllithium in presence of copper(I) iodide in THF is used for alkylation. If an excess of the lithium derivative is present, introduction of oxygen or air can cause a violent explosion, even at —78°C.

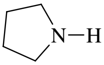
2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine

Harris, R. *et al., J. Chem. Soc., Dalton Trans.*, 1976, 23

Interaction in hexane to produce the 2,4-di-*tert*-butyl derivative often starts only after an induction period and may then proceed very violently. Careful temperature control is imperative.

See other ALKYLMETALS, INDUCTION PERIOD INCIDENTS

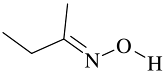
†1648. Pyrrolidine
[123-75-1] **C_4H_9N**



Benzaldehyde, Propionic acid

See Benzaldehyde: Propionic acid, etc.

1649. 2-Butanone oxime (2-Oximinobutane)
[96-29-7] **C_4H_9NO**



HCS 1980, 652

Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3

Investigation following two violent explosions involving the oxime or its derivatives showed that it may be distilled at 152°C at ambient pressure only if highly purified. Presence of impurities, especially acidic impurities (e.g. the oxime hydrochloride) drastically lowers the temperature at which degradation occurs.

See 2-Butanone oxime hydrochloride

See other CATALYTIC IMPURITY INCIDENTS

Sulfuric acid

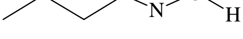
MCA Guide, 1972, 300

The oxime was hydrolysed with aqueous sulfuric acid and the 2-butanone liberated was distilled out at 15 mbar from a bath at 110—115°C. Soon after release of vacuum and bath removal, the residue (crude hydroxylaminium sulfate) decomposed violently.

See HYDROXYLAMINIUM SALTS

See other OXIMES

1650. Butyraldehyde oxime (1-Hydroxyiminobutane)
[151-00-8] **C_4H_9NO**



1. Anon., *Sichere Chemiearb.*, 1966, **18**(3), 20
2. Kröger, —, *Proc. 1st Int. Symp. Prev. Occ. Risks Chem. Ind.*, 180—187, Heidelberg, ISSA, 1970

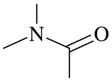
A large batch exploded violently (without flame) during vacuum distillation at 90—100°C/20—25 mbar. Since the distilled product contained up to 12% butyronitrile, it was assumed that the the oxime had undergone the Beckman rearrangement to butyramide and then dehydrated to the nitrile. The release of water into a system at 120°C would generate excessive steam pressure which the process vessel could not withstand. The rearrangement may have been catalysed by metallic impurities [1]. This hypothesis was confirmed in a detailed study, which identified lead oxide and rust as active catalysts for the rearrangement and dehydration reactions [2].

Sulfuric acid: Cyclopentanone oxime

See Ethyl 2-formylpropionate oxime: Hydrogen chloride

See other CATALYTIC IMPURITY INCIDENTS, OXIMES

1651. ***N,N*-Dimethylacetamide**
[127-19-5] **C_4H_9NO**



HCS 1980, 420

Halogenated compounds

1. 'DMAC Brochure A-79931', Wilmington, Du Pont, 1969
2. Cardillo, P. *et al., 3rd Euro. Symp. Therm. Anal. Calorim.*, Interlaken, 1984 (private comm.,)

The tertiary amide acts as a dehydrohalogenating agent, and reaction with some highly halogenated compounds (carbon tetrachloride, hexachlorocyclohexane) is very exothermic and may become violent, particularly if iron is present [1]. A detailed investigation by ARC shows that 1:1 w/w mixtures with carbon tetrachloride are most reactive and that 2 exotherms are evident. One starting at 91° and ending at 97°C is relatively weak (40 J/g) while the second, starting at 97° and ending at 172° has its maximum rate at 147°C, with an exotherm of 508 J/g, which under adiabatic runaway conditions would give a final temperature exceeding 450°C. A considerable release of gas generates a maximum pressure of 12.8 bar at 172°C. Presence of 1% of iron powder initiates the first exotherm at 71°C and increases it to 60 J/g, the second exotherm being marginally reduced by presence of iron. The exothermic effect is much greater than in the similar reactions of DMF [2].

See Carbon tetrachloride: Dimethylformamide

See 3,4-Dichloronitrobenzene

See Sodium hydride, dimethylformamide

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

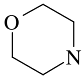
Other reactants

Yoshida, 1980, 165

MRH values calculated for 13 combinations with oxidants are given.

See other APROTIC SOLVENTS

1652. Morpholine (Tetrahydro-1,4-oxazine)
[110-91-8] **C_4H_9NO**



HCS 1980, 671; *RSC Lqab. Hazards Data Sheet No. 73*, 1988

Cellulose nitrate

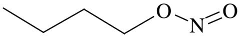
See CELLULOSE NITRATE: AMINES

Nitromethane

See Nitromethane: Acids, etc.

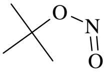
See other ORGANIC BASES

†1653. Butyl nitrite
[544-16-1] **$C_4H_9NO_2$**



See other ALKYL NITRITES

†1654. *tert*-Butyl nitrite
[540-80-7] **$C_4H_9NO_2$**



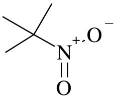
Lopez, F., *Chem. Eng. News*, 1992, **70**(51), 2

DSC showed that exothermic decomposition (—1200 J/g) begins at about 110°C. A falling hammer test indicated shock induced decomposition. Considerable caution is advised when employing this useful reagent.

See DIFFERENTIAL SCANNING CALORIMETRY

See other ALKYL NITRITES

1655. *tert*-Nitrobutane (2-Methyl-2-nitropropane)
[594-70-7] **$C_4H_9NO_2$**



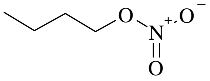
Preparative hazard

Mee, A. J., *School Sci. Rev.*, 1940, **22**(85), 96

A sample exploded during distillation.

See Potassium permanganate: Acetone, *tert*-Butylamine
See other NITROALKANES

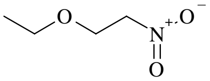
1656. Butyl nitrate
[928-45-0] **$C_4H_9NO_3$**



Lewis acids
See other ALKYL NITRATES: Lewis acids

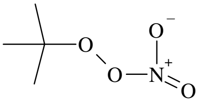
Other reactants
Yoshida, 1980, 203
MRH values calculated for 10 combinations with various reagents are given.
See other ALKYL NITRATES

1657a. Ethyl 2-nitroethyl ether (2-Nitroethoxyethane)
[31890-52-5] **$C_4H_9NO_3$**



Cann, P. F. *et al., J. Chem. Soc., Perkin Trans. 2*, 1974, 817—819
Addition of diphenyl ether as an inert diluent to the crude ether before distillation at 0.13 mbar is essential to prevent violent explosion of the residue after it has cooled.
See related NITROALKANES

1657b. *tert*-Butyl peroxynitrate (1,1-Dimethylethyl peroxynitrate)
[ ] **$C_4H_9N)_4$**

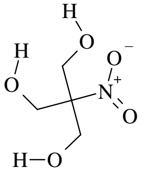


Like other low molecular weight peroxyesters, or alkylnitrates, this is a material to avoid isolating even when you can make it.

Preparative hazard
See tert-Butylhydroperoxide: Toluene, Dinitrogen pentaoxide
See other PEROXYESTERS

1658. Tris(hydroxymethyl)nitromethane (2-Hydroxymethyl-2-nitropropane-1,3-diol)

[126-11-4] **$C_4H_9NO_5$**



Hydrogen, Nickel

Ostis, K. *et al., Chem. Abs.*, 1975, **82**, 36578

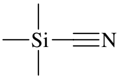
Catalytic hydrogenation of the title compound to the amine with hydrogen at 5—10 bar is described as hazardous, and an electrochemical reduction process is recommended.

See other CATALYTIC NITRO REDUCTION PROCESSES, HYDROGENATION INCIDENTS

See related NITROALKANES

†1659. Cyanotrimethylsilane

[7677-24-9] **C_4H_9NSi**

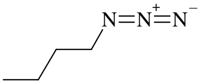


See other CYANO COMPOUNDS

See related ALKYLHALOSILANES

1660. 1-Azidobutane (Butyl azide)

[7332-00-5] **$C_4H_9N_3$**

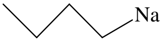


See Butyl toluenesulfonate

See AZIDES

1661a. Butylsodium

[3525-44-8] **C_4H_9Na**

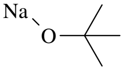


Preparative hazard

See SODIUM: 1-Chlorobutane

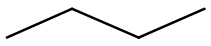
See other ALKYLMETALS

1661b. Sodium *tert*-butoxide (Sodium 2-Methyl-2-propoxide)
[13259-29-5] **C_4H_9NaO**



See Butyllithium: Sodium tert-butoxide, Dimethyl sulfide

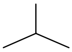
†1662. Butane
[106-97-8] **C_4H_{10}**



FPA H15, 1973 (cylinder); *HCS 1980*, 224 (cylinder)

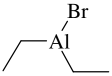
See LIQUEFIED PETROLEUM GASES

†1663. Isobutane (2-Methylpropane)
[75-28-5] **C_4H_{10}**



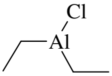
FPA H119, 1983 (cylinder); *HCS 1980*, 565

1664. Diethylaluminium bromide
[760-19-0] **$C_4H_{10}AlBr$**



Nitromethane
See Nitromethane: Alkylmetal halides
See entry ALKYLALUMINIUM HALIDES

1665. Diethylaluminium chloride
[96-10-6] **$C_4H_{10}AlCl$**

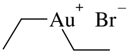


HCS 1980, 390

Chlorine azide
Houben-Weyl 1970, Vol. 13.4, 76
Interaction produces distillable ethylaluminium azide chloride, but the residue is explosive.
See other ALKYLALUMINIUM HALIDES

1666. Diethylgold bromide

[26645-10-3] **$C_4H_{10}AuBr$**



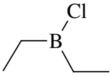
Sorbe, 1968, 63

It explodes at 70°C.

See other ALKYLMETAL HALIDES, GOLD COMPOUNDS

1667. Chlorodiethylborane

[5314-83-0] **$C_4H_{10}BCl$**



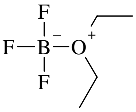
Koster, R. *et al., Inorg. Synth.*, 1974, **15**, 149—152

It ignites in air; preparative hazard also described.

See other ALKYLHALOBORANES

1668. Boron trifluoride diethyl etherate

[109-63-7] **$C_4H_{10}BF_3O$**



HCS 1980, 217

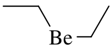
Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Boron trifluoride diethyl etherate

See related NON-METAL HALIDES

1669. Diethylberyllium

[542-63-2] **$C_4H_{10}Be$**



Air, or Water

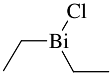
Coates, 1967, Vol. 1, 106

Ignites in air, even when containing ether, and reacts explosively with water.

See other ALKYLMETALS

1670. Diethylbismuth chloride

[65313-34-0] **$C_4H_{10}BiCl$**



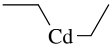
Gilman, H. *et al., J. Org. Chem.*, 1939, **4**, 167

It ignites in air.

See other ALKYLMETAL HALIDES

1671. Diethylcadmium

[592-02-9] **$C_4H_{10}Cd$**



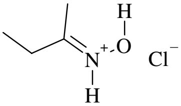
1. Krause, E., *Ber.*, 1918, **50**, 1813
2. Houben-Weyl, 1973, Vol. 13.2a, 903 (footnote 3), 908

The vapour decomposes explosively at 180°C. Exposure to ambient air produces white fumes which turn brown and then explode violently [1]. Moderate quantities decompose explosively when heated rapidly to 130, not 180°C as stated previously. This, apart from allylcadmium derivatives, is the only pyrophoric dialkylcadmium [2] (but *see* Dimethylcadmium). It is mildly endothermic (ΔH_f° (l) +61.5 kJ/mol, 0.36 kJ/g).

See other ALKYLMETALS, ENDOTHERMIC COMPOUNDS

1672. 2-Butanone oxime hydrochloride (2-Hydroxyliminiobutane chloride)

[4154-69-2] **$C_4H_{10}ClNO$**



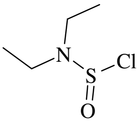
Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3

The salt undergoes violent degradation at 50—70°C, and its presence in trace quantities may promote degradation of the oxime.

See related OXIMES

1673. Diethylaminosulfinyl chloride

[34876-30-7] **$C_4H_{10}ClNOS$**



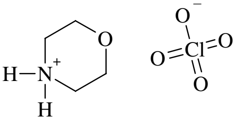
Preparative hazard

See Sulfinyl chloride: Bis(dimethylamino) sulfoxide

See other N—S COMPOUNDS

1674. Morpholinium perchlorate

[35175-75-8] **$C_4H_{10}ClNO_5$**



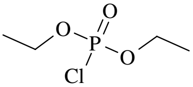
Udupa, M. R., *Thermochim. Acta*, 1980, **38**, 241—143

It decomposes exothermally at 230°C.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

1675. Diethyl phosphorochloridate (Diethyl chlorophosphate)

[814-49-3] **$C_4H_{10}ClO_3P$**



Silbert, L. A., *J. Org. Chem.*, 1971, **36**, 2162

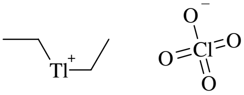
Presence of hydrogen chloride as impurity causes an uncontrollable exothermic reaction during preparation of diethyl phosphate from the title compound.

See other CATALYTIC IMPURITY INCIDENTS

See related PHOSPHORUS ESTERS

1676. Diethylthallium perchlorate

[22392-07-0] (ion) **$C_4H_{10}ClO_4Tl$**



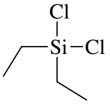
Cook, J. R. *et al., J. Inorg. Nucl. Chem.*, 1964, **26**, 1249

It explodes at the m.p., 250°C.

See related METAL PERCHLORATES

†1677. Dichlorodiethylsilane

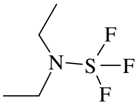
[1719-53-5] **$C_4H_{10}Cl_2Si$**



See other ALKYLHALOSILANES

1678. Diethylaminosulfur trifluoride

[38078-09-0] **$C_4H_{10}F_3NS$**



Alone, or Water

1. Cochran, J., *Chem. Eng. News*, 1979, **57**(12), 4, 74
2. Middleton, W. J., *Chem. Eng. News*, 1979, **57**(21), 43
3. Middleton, W. J. *et al., J. Org. Chem.*, 1980, **45**, 2884 (footnote 3)
4. Middleton, W. J. *et al., Org. Synth.*, 1977, **57**, 50
5. Breckenridge, R. J. *et al., Chem. Brit.*, 1982, **18**, 619
6. Suckling, C. J., private comm., 1982
7. Pivawer, P. M., private comm., 1983

Explosive decomposition occurred when stripping solvent or attempting vacuum distillation. Exothermic decomposition begins at about 50°C and is violent above 90°C. Contact with water causes explosive decomposition [1]. Later comments suggest that the compound may be distilled safely at pressures below 13 mbar and handled safely in solution, or in bulk below 50°C [2,3]. While repeating an earlier procedure [4], two explosions occurred. One was when admitting air to the residue from vacuum distillation, and the second immediately prior to redistillation of the cold product from vacuum stripping of solvent [5]. This was attributed to formation of some impurities related to a dialkylaminofluorosulfur imine [6]. During preliminary distillation to remove sulfur tetrafluoride, etc., the line from the cold trap to the alkaline scrubber must end in an inverted funnel to avoid blockage with solid [7].

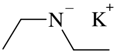
See S-Diethylamino(methylimino)sulfur(IV) fluoride

See other N—S COMPOUNDS

See related NON-METAL HALIDES

1679. Potassium diethylamide

[2245-68-3] **$C_4H_{10}KN$**



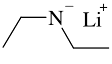
Pez, G. P. *et al., Pure Appl. Chem.*, 1986, **57**, 1925

The solid is highly pyrophoric and will react violently even with limited exposure to air

See other N-METAL DERIVATIVES, PYROPHORIC MATERIALS

1680. Lithium diethylamide

[816-43-3] **$C_4H_{10}LiN$**



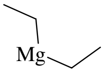
1. Fischer, E. O. *et al., Inorg. Synth.*, 1979, **19**, 165
2. Pez, G. P. *et al., Pure Appl. Chem.*, 1986, **57**, 1924

Extremely pyrophoric in air [1], and will react violently upon even brief contact [2].

See other N-METAL DERIVATIVES, PYROPHORIC MATERIALS

1681. Diethylmagnesium

[557-18-6] **$C_4H_{10}Mg$**



Air, or Water

Gilman, H. *et al., J. Amer. Chem. Soc.*, 1930, **52**, 5048

Contact with moist air usually caused ignition of the dry powder, and water always ignited the solid or its ethereal solution.

Carbon dioxide

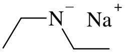
Merck, 1983, 453

It will glow and ignite in carbon dioxide.

See other ALKYLMETALS, DIALKYLMAGNESIUMS

1682. Sodium diethylamide

[34992-80-8] **$C_4H_{10}NNa$**



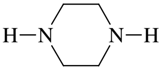
Pez. G. P. *et al., Pure Appl. Chem.*, 1986, **57**, 1925

The solid is highly pyrophoric and will react violently even on limited exposure to air.

See other N-METAL DERIVATIVES, PYROPHORIC MATERIALS

1683. Piperazine (Hexahydropyrazine)

[110-85-0] **$C_4H_{10}N_2$**



HCS 1980, 756

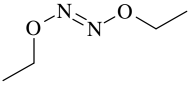
Dicyanofurazan

See Dicyanofurazan: Nitrogenous bases

See other ORGANIC BASES

1684. Diethyl hyponitrite (Diethoxydiazene)

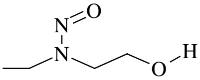
[4549-46-6] **$C_4H_{10}N_2O_2$**



See entry DIALKYL HYPONITRITES

1685. *N*-Nitrosoethyl-2-hydroxyethylamine

[13147-25-6] **$C_4H_{10}N_2O_2$**



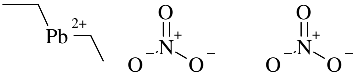
Preussman, R., *Chem. Ber.*, 1962, **95**, 1572

It decomposed explosively during attempted distillation at 18 mbar from a bath at 170°C, but was distilled with slight decomposition at 103—105°/0.4 mbar.

See other NITROSO COMPOUNDS

1686. Diethyllead dinitrate

[17498-10-1] **$C_4H_{10}N_2O_6Pb$**



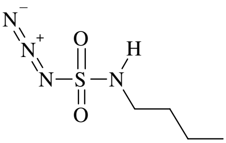
Potts, D. *et al., Can. J. Chem.*, 1969, **47**, 1621

The salt is unstable above 0°C and explodes on heating.

See related ALKYLMETALS, HEAVY METAL DERIVATIVES

1687. *N*-Butylamidosulfuryl azide

[13449-22-4] **$C_4H_{10}N_4O_2S$**

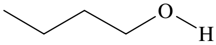


Shozda, R. J. *et al., J. Org. Chem.*, 1967, **32**, 2876

It exploded during analytical combustion.

See other ACYL AZIDES

1688. 1-Butanol
[78-83-1] **$C_4H_{10}O$**



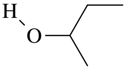
FPA H64, 1977; *HCS 1980*, 236

Aluminium MRH 1.17/11
See Aluminium: Butanol

Chromium trioxide MRH 2.55/92
See Chromium trioxide: Alcohols

Other reactants
Yoshida, 1980, 297
MRH values calculated for 15 combinations, largely with oxidants, are given.

†1689. 2-Butanol
[78-92-2] **$C_4H_{10}O$**



HCS 1980, 237

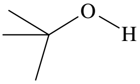
1. Posdev, V. S. *et al., Chem. Abs.*, 1977, **86**, 194347
2. Peterson, D., *Chem. Eng. News*, 1981, **59**(19), 3
3. Sharpless, T. W., *J. Chem. Educ.*, 1984, **61**, 476
4. Doyle, R. R., *Chem. Eng. News*, 1986, **64**(7), 4: *J. Chem. Educ.*, 1986, **63**(20, 186)

A powerful explosion which occurred during distillation of a 10-year-old sample of the alcohol was attributed to presence of peroxy compounds formed by autoxidation, possibly involving 2-butanone as an effective photochemical sensitiser [1]. After a later explosion, it was found that the sample being distilled contained 12% of peroxide [2]. A further incident involved a 12-year old sample which exploded at the end of distillation, and which also contained a high level of peroxide. Several other stock alcohols were found to contain much lower levels of peroxide than the 2-butanol, and recommendations on clean-up or disposal, depending on the level of peroxide, are made [3]. A further report of an explosion at the end of laboratory distillation confirms the potential for peroxide formation on prolonged storage of 2-butanol [4].
See 2-Propanol: 2-Butanone

Chromium trioxide
See Chromium trioxide: Alcohols
See other PEROXIDISABLE COMPOUNDS

†1690. *tert*-Butanol

[75-65-0] **$C_4H_{10}O$**



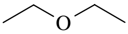
HCS 1980, 238

Potassium—sodium alloy

See Potassium—sodium alloy: *tert*-Butanol

†1691. Diethyl ether (Ethoxyethane)

[60-29-7] **$C_4H_{10}O$**



(*MCA SD-29*, 1965); *NSC 396*, 1968; *FPA H40*, 1975; *HCS 1980*, 487; *RSC Lab. Hazards Data Sheet No. 48*, 1965

1. Criegee, R. *et al., Angew. Chem.*, 1936, **49**, 101
2. Criegee, R. *et al., Angew. Chem.*, 1958, **70**, 261
3. Mallinckrodt, E. *et al., Chem. Eng. News*, 1955, **33**, 3194
4. Ray, A., *J. Appl. Chem.*, 1955, 188
5. Anon., *Chemist & Druggist*, 1947, **157**, 258
6. Feinstein, R. N., *J. Org. Chem.*, 1959, **24**, 1172
7. Davies, A. G., *J. R. Inst. Chem.*, 1956, **80**, 386
8. Anon., *Lab. Accid. in Higher Educ.*, Item 27, HSE, Barking, 1987
9. Ceru, B., *Safe Science* (Michigan State University), 1995, July

The hydroperoxide initially formed by autoxidation of ether is not particularly explosive, but on standing and evaporation, polymeric 1-oxyperoxides are formed which are dangerously explosive, even below 100°C [1]. Numerous laboratory explosions have been caused by evaporation of peroxidised ether [2]. Formation of peroxide in stored ether may be prevented by presence of sodium diethyldithiocarbamate (0.05 ppm), [4], which probably deactivates traces of metals which catalyse peroxidation [2]; of pyrogallol (1 ppm) [4]; or by larger proportions (5 to 20 ppm) of other inhibitors [5]. Once present in ether, peroxides may be detected by the iodine—starch test, and removed by percolation through anion exchanger resin [6] or activated alumina [7], which leaves the ether dry, or by shaking with aqueous ferrous sulfate or sodium sulfite solutions. Many other methods have been described [7]. A small quantity of ether stored in an unmodified domestic refrigerator in a biochemistry laboratory led to an explosion, with ignition by the thermostat contacts [8]. An explosion attributed to peroxide formation is reported during a laboratory clear-up. It happened a few seconds after antique ether containers, in a fume hood with other materials, were opened; too long for mechanical initiation of peroxide explosion and not long enough for concentration by evaporation of ether. The main injuries were nitric acid burns [9]. (Since clear-ups are a common time for mixing nitric acid with waste solvent, the attribution may be suspect.)

See 1-OXYPEROXY COMPOUNDS
See other PEROXIDISABLE COMPOUNDS, POLYPEROXIDES

Boron triazide
See Boron triazide: Diethyl ether, etc.

Halogens, or Interhalogens
See Bromine trifluoride: Halogens, etc., or: Solvents
Bromine pentafluoride: Hydrogen-containing materials
Bromine: Diethyl ether
Chlorine: Diethyl ether
Iodine heptafluoride: Organic solvents

Other reactants
Yoshida, 1980, 140
MRH values calculated for 13 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Halogens, or Interhalogens, above	
Chromyl chloride: Organic solvents	
'Fluorine nitrate': Organic materials	
Hydrogen peroxide: Diethyl ether	MRH 6.53/84
Iodine(VII) oxide: Diethyl ether	
LIQUID AIR: Diethyl ether	
Lithium perchlorate: Diethyl ether	
Nitric acid: Diethyl ether	MRH 5.94/79
Nitrosyl perchlorate: Organic materials	
Nitryl perchlorate: Organic solvents	
Ozone: Diethyl ether	
Perchloric acid: Diethyl ether	
Permanganic acid: Organic materials	
Peroxodisulfuric acid: Organic liquids	
Silver perchlorate: Diethyl ether	
Sodium peroxide: Organic liquids	MRH 2.55/92

Peat soils
Walkley, A., *Austral. Chem. Inst. J.*, 1939, **6**, 310
Explosions occurred during the extraction of fats and waxes from the soils with ether, as well as when heating the extract at 100°C. Although the latter is scarcely surprising (the ether contained 230 ppm of peroxides), the former observation is unusual.

Sulfur, or Sulfur compounds
See Sulfonyl chloride: Diethyl ether
Sulfur: Diethyl ether
Thiotrithiazyl perchlorate: Organic solvents

Uranyl nitrate
See Uranyl nitrate: Diethyl ether

Wood pulp extracts

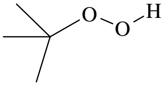
Durso, D. F., *Chem. Eng. News*, 1957, **35**(34), 91, 115

Ethereal extracts of pulp exploded during or after concentration by evaporation. Although the ether used for the extraction previously had been freed from peroxides by treatment with cerium(III) hydroxide, the ethereal extracts had been stored for 3 weeks before concentration was effected. (During this time the ether and/or extracted terpenes would be expected to again form peroxides, but no attempt seems to have been made to test for, or to remove them before distillation was begun).

See other PEROXIDISABLE COMPOUNDS

1692. *tert*-Butyl hydroperoxide (2-Hydroperoxy-2-methylpropane)

[75-91-2] **$C_4H_{10}O_2$**



1. Milas, N. A. *et al., J. Amer. Chem. Soc.*, 1946, **68**, 205
2. Castrantas, 1965, 15
3. Sharpless, K. B. *et al., Aldrichimica Acta*, 1979, **12**, 63—73
4. Verhoeff, J., *Runaway Reactions*, 1981, Paper 3/T, 1—12
5. Hill, J. H. *et al., J. Org. Chem.*, 1983, **48**, 3607—3608

Though relatively stable, explosions have been caused by distillation to dryness [1], or attempted distillation at ambient pressure [2]. In a comprehensive review of the use of the hydroperoxide as a selective metal-catalysed oxygenator for alkenes and alkynes, attention is drawn to several potential hazards in this application. One specific hazard to be avoided stems from the fact that Lucidol TBHP-70 contains 19% of di-*tert*-butyl peroxide which will survive the catalysed reaction and may lead to problems in the work-up and distillation [3]. A thorough investigation of the stability and explosive properties of the 70% solution in water has been carried out [4]. The anhydrous peroxide as a solution in toluene may now readily be prepared azeotropically, and the solutions are stable in storage at ambient temperature. This solution is now a preferred method for using the anhydrous hydroperoxide [5].

See 1,2-Dichloroethane, below

See also THERMAL EXPLOSIONS

Acids

1. Sharpless, K. B. *et al., Aldrichimica Acta*, 1979, **12**, 71
2. Andreozzi, R. *et al., J. Haz. Mat.*, 1988, **17**, 305—313

Not even traces of strong acids should be added to high strength solutions of the hydroperoxide [1]. The thermal stability and mechanism of cleavage of mixtures with 4-toluenesulfonic acid have been studied under adiabatic conditions, and there is potential for development of a thermal runaway [2].

1,2-Dichloroethane

Hill, J. H. *et al., J. Org. Chem.*, 1983, **48**, 3607

Solutions of the hydroperoxide in halogenated solvents, and especially dichloroethane are much less stable than in toluene (reference 5 above). On a large scale, the azeotropic drying of solutions of the hydroperoxide in dichloroethane may present a thermal hazard.

Molecular sieves

Sharpless, K. B. *et al., Aldrichimica Acta*, 1979, **12**, 71

Use of the 4A sieve to dry the hydroperoxide (6% water) had been used routinely without incident, but inadvertent use of the larger-pored 13X sieve gave a high exotherm in the packed bed which soon led to autoignition of the hydroperoxide. This was attributed to the heat of adsorption occurring within the larger sieve pores (10 Angstroms in 13X), but caution is advised when using sieve to dry any high strength (90%) solutions of the hydroperoxide, and an azeotropic method is preferred (see reference 5 above).

See Nitromethane: Molecular sieve

See other MOLECULAR SIEVE INCIDENTS

Preparative hazard

See Hydrogen peroxide: *tert*-Butanol, Sulfuric acid

Toluene, Dinitrogen pentaoxide

1. Owens, K. A. *et al., J. Loss Prevention*, 1995, **8**(5), 296
2. Editor's comments

Toluene was used, in place of tetrachloromethane, as solvent when preparing *t*-Butyl peroxynitrate. An explosion ensued, attributed to trinitrotoluene formation and detonation [1]. Since TNT is not easy to form and difficult to explode, this seems improbable. The intended product will certainly be a more dangerous explosive than TNT, as can be the expected byproduct, an unreacted solution of anhydrous nitric acid in toluene. Most explosions in nitration systems are due to free radical oxidation of an organic substrate or solvent by the nitrating agent; this is quite probable here. Though nitrogen pentoxide is itself more an ionic nitration reagent than a radical oxidant, all peroxy species are radical generators par excellence, and commonly used to initiate free radical reaction sequences [2].

Transition metal salts

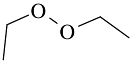
1. Sharpless, K. B. *et al., Aldrichimica Acta*, 1979, **12**, 71
2. Weinmann, H. *et al. Org. Process R. & D.*, 1998, **2**, 100

Transition metal salts known to be good autoxidation catalysts (of cobalt, iron or manganese) should never be added to high-strength solutions of the hydroperoxide to avoid the near-certainty of vigorous evolution of a large volume of oxygen [1]. A detailed account has been given of the scale-up, and associated safety studies, of the allylic oxidation of steroids to enones by ruthenium catalysed butyl hydroperoxide to multi-kilogram scale [2].

SCALE OF WORK

See other ALKYL HYDROPEROXIDES

1693. Diethyl peroxide
[628-37-5] **$C_4H_{10}O_2$**

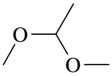


1. Baeyer, A. *et al., Ber.*, 1900, **33**, 3387
2. Castrantas, 1965, 15
3. Baker, G. *et al., Chem. & Ind.*, 1964, 1988
4. Gray, P. *et al., Proc. R. Soc.*, 1971, **A325**, 175

While it is acknowledged as rather explosive, the stated lack of shock-sensitivity at ambient temperature [1] is countered by its alternative description as shock-sensitive [2] and detonable [3]. The vapour explodes above a certain critical pressure, at temperatures above 190°C [4].

See other DIALKYL PEROXIDES

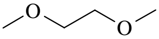
†1694. 1,1-Dimethoxyethane
[534-15-6] **$C_4H_{10}O_2$**



HCS 1980, 417

See other PEROXIDISABLE COMPOUNDS

†1695. 1,2-Dimethoxyethane
[110-71-4] **$C_4H_{10}O_2$**

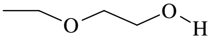


HCS 1980, 418

Phifer, L. H., *CHAS Notes*, 1982, **1**(3), 2
A seven-year-old peroxidised sample exploded during distillation.

Lithium tetrahydroaluminate
See Lithium tetrahydroaluminate: 1,2-Dimethoxyethane
See other PEROXIDISABLE COMPOUNDS

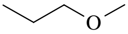
1696. 2-Ethoxyethanol
[110-80-5] **$C_4H_{10}O_2$**



HCS 1980, 459

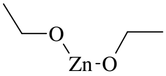
Hydrogen peroxide, Poly(acrylamide) gel, etc.
See Hydrogen peroxide: 2-Ethoxyethanol, etc.
See other PEROXIDISABLE COMPOUNDS

†1697. Methyl propyl ether (1-Methoxypropane)
[557-17-5] **$C_4H_{10}O_2$**



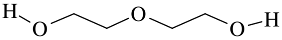
HCS 1980, 660

1698. Zinc ethoxide
[3851-22-7] **$C_4H_{10}O_2Zn$**



Nitric acid
Solomartin, V. S. *et al., Chem. Abs.*, 1977, **87**, 210678
In the analysis of diethylzinc, a 1 ml sample is cooled to —196°C and treated with 2 ml of ethanol to give the ethoxide. During subsequent conversion to zinc nitrate (prior to pyrolysis to the oxide) by treatment with 3 ml of 30% nitric acid, cooling must be continued to avoid an explosion hazard.
See other METAL ALKOXIDES

1699. Bis(2-hydroxyethyl) ether (Diethylene glycol)
[111-46-6] **$C_4H_{10}O_3$**

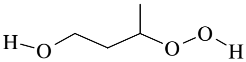


HCS 1980, 397

Other reactants
Yoshida, 1980, 144
MRH values calculated for 14 combinations, largely with oxidants, are given.

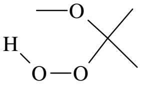
Sodium hydroxide
See Sodium hydroxide: Glycols

1700. 1-Hydroxy-3-butyl hydroperoxide (3-Hydroperoxy-1-butanol)
[ ] **$C_4H_{10}O_3$**



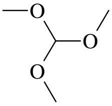
Rieche, A., *Ber.*, 1930, **63**, 2462
It explodes on heating.

1701. 2-Methoxyprop-2-yl hydroperoxide (2-Methoxy-1-methylethyl hydroperoxide)
[10027-74-4] **$C_4H_{10}O_3$**



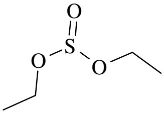
Dussault, P., *Chem. Eng. News*, 1993, **71**(32), 2
This reagent, made by methanolic ozonolysis of tetramethylethylene, may deflagrate if isolated.
See Hydrogen peroxide: Acetone
See related 1-OXYPEROXY COMPOUNDS

†1702. Trimethyl orthoformate (Trimethoxymethane)
[149-73-5] **$C_4H_{10}O_3$**



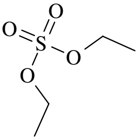
Preparative hazard
See Chloroform: Sodium, Methanol, or: Sodium methoxide

1703. Diethyl sulfite
[623-81-4] **$C_4H_{10}O_3S$**



Chlorine fluoride
See Ethyl fluorosulfate
See other SULFUR ESTERS

1704. Diethyl sulfate
[64-67-5] **$C_4H_{10}O_4S$**



HCS 1980, 406

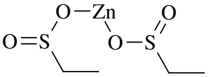
3,8-Dinitro-6-phenylphenanthridine, Water
Hodgson, J. F., *Chem. & Ind.*, 1968, 1399

Accidental ingress of water to the heated mixture liberated sulfuric acid or its half ester which caused a violent reaction with generation of a large volume of solid black foam.
See 4-Nitroaniline-2-sulfonic acid
See also Sulfuric acid: Nitroaryl bases, etc.

Iron, Water
Siebeneicher, K., *Angew. Chem.*, 1934, **47**, 105
Moisture in a sealed iron drum of the ester caused hydrolysis to sulfuric acid, leading to corrosion of the metal and development of a high internal pressure of hydrogen, which ruptured the drum.
See other CORROSION INCIDENTS, GAS EVOLUTION INCIDENTS

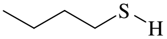
Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.
See other SULFUR ESTERS

1705. Zinc ethylsulfinate
[24308-92-7] **$C_4H_{10}O_4S_2Zn$**



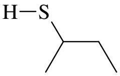
Preparative hazard
See Diethylzinc: Sulfur dioxide
See related SULFUR ESTERS

†1706. Butanethiol
[109-79-5] **$C_4H_{10}S$**



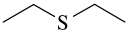
Nitric acid
See Nitric acid: Alkanethiols
See other ALKANETHIOLS

†1707. 2-Butanethiol
[513-53-1] **$C_4H_{10}S$**



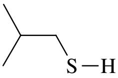
See other ALKANETHIOLS

†1708. Diethyl sulfide (3-Thiapentane)
[352-93-2] **$C_4H_{10}S$**



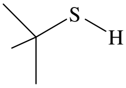
HCS 1980, 407

†1709. 2-Methylpropanethiol
[513-44-0] **$C_4H_{10}S$**



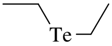
Calcium hypochlorite
See Calcium hypochlorite: Organic sulfur compounds
See other ALKANETHIOLS

†1710. 2-Methyl-2-propanethiol
[75-66-1] **$C_4H_{10}S$**



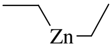
See other ALKANETHIOLS

1711. Diethyl telluride
[627-54-3] **$C_4H_{10}Te$**



Ellern, 1968, 24—25
It ignites in air.
See other ALKYLMETALS

1712. Diethylzinc
[557-20-0] **$C_4H_{10}Zn$**



Aluminium Alkyls and other Organometallics, 5, New York, Ethyl Corp., 1967

It is immediately pyrophoric in air.

Alkenes, Diiodomethane

1. Houben-Weyl, 1973, Vol. 13.2a, 845
2. www2.umdnj.edu/eohssweb/aiha/accidents/explosion. 2002, American Industrial Hygiene Association
3. Editor's Comment

During preparation of cyclopropane derivatives, it is important to add the diiodomethane slowly to a solution of diethylzinc in the alkene. Addition of diethylzinc to an alkene—diiodomethane mixture may be explosively violent [1]. A modified procedure whereby the zinc alkyl and diiodomethane are mixed in dichloromethane solvent, allowed to react and the alkene then added last, normally forms a dispersed precipitate prior to alkene addition. During such an experiment the magnetic stirrer stopped and a settled precipitate formed. Attempting to restart the mixing caused detonation. Various improbable causes are considered [2]. Any such procedure must be forming halomethylzinc species as intermediates. These will be high energy and consequently dangerous as a bulk solid [3].

See other MAGNETIC STIRRERS

Dihalomethanes

See other Alkenes, Diodomethane, above

Halogens

See Bromine: Diethylzinc
Chlorine: Diethylzinc

Methanol

Houben-Weyl, 1973, Vol. 13.2a, 855

Interaction is explosively violent and ignition ensues.

Nitro compounds

Leleu, *Cahiers*, 1977, (88), 371

Interaction is usually violent.

Non-metal halides

Leleu, *Cahiers,* 1977, (88), 372

Interaction with arsenic trichloride or phosphorus trichloride is violent, forming pyrophoric triethylarsine or triethylphosphine.

Ozone

See Ozone: Alkylmetals

Sulfur dioxide

Houben-Weyl, 1973, 13.2a, 709

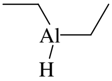
During preparation of zinc ethylsulfinate, addition of diethylzinc to liquid sulfur dioxide at —15°C leads to an explosively violent reaction. Condensation of sulfur dioxide into cold diethylzinc leads to a controllable reaction on warming.

Water

Ito, Y. *et al., Org. Synth.*, 1979, **59**, 113, 116

It reacts violently with water, but a procedure for destroying excess reagent with ice-water is detailed.
See other ALKYLMETALS, DIALKYLZINCS

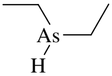
1713. Diethylaluminium hydride
[871-27-2] **$C_4H_{11}Al$**



HCS 1980, 391

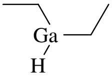
See entry ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

1714. Diethylarsine
[692-42-2] **$C_4H_{11}As$**



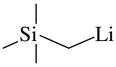
Sidgwick, 1950, 762
It ignites in air, even at 0°C.
See other ALKYLNON-METAL HYDRIDES

1715. Diethylgallium hydride (Diethylhydrogallium)
[93481-56-2] **$C_4H_{11}Ga$**



Air, or Water
Eisch, J. J., *J. Amer. Chem. Soc.*, 1962, **84**, 3835
It ignites in air, and reacts violently with water.
See other ALKYLMETAL HYDRIDES

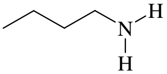
1716. Trimethylsilylmethyllithium
[1872-00-0] **$C_4H_{11}LiSi$**



Tessier-Youngs, C. *et al., Inorg. Synth.*, 1986, **24**, 92
It ignites spontaneously in air and reacts violently with water, like the aluminium analogue.
See related ALKYLMETALS, ALKYLSILANES

†1717. Butylamine (1-Aminobutane)

[109-73-9] **$C_4H_{11}N$**



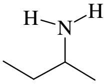
FPA H100, 1982; *HCS 1980*, 239

Other reactants
Yoshida, 1980, 305
MRH values calculated for 13 combinations with oxidants are given.

Perchloryl fluoride
See Perchloryl fluoride: Nitrogenous bases
See other ORGANIC BASES

†1718. 2-Butylamine (2-Aminobutane)

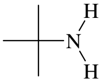
[13952-84-6] **$C_4H_{11}N$**



See other ORGANIC BASES

†1719. *tert*-Butylamine (2-Amino-2-methylpropane)

[75-64-9] **$C_4H_{11}N$**

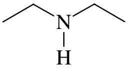


HCS 1980, 240

2,2-Dibromo-1,3-dimethylcyclopropanoic acid
See 2,2-Dibromo-1,3-dimethylcyclopropanoic acid: *tert*-Butylamine
See other ORGANIC BASES

†1720. Diethylamine

[109-89-7] **$C_4H_{11}N$**



(*MCA SD-97*, 1971); *FPA H85*, 1979; *HCS 1980*, 392

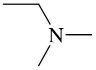
Cellulose nitrate
See CELLULOSE NITRATE: AMINES

Dicyanofurazan
See Dicyanofurazan: Nitrogenous bases

Other reactants
Yoshida, 1980, 139
MRH values calculated for 13 combinations with oxidants are given.

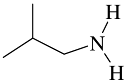
Sulfuric acid
See Sulfuric acid: Diethylamine
See other ORGANIC BASES

†1721. Ethyldimethylamine
[598-56-1] **$C_4H_{11}N$**



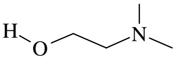
See other ORGANIC BASES

†1722. Isobutylamine (2-Methypropylamine)
[78-81-9] **$C_4H_{11}N$**



See other ORGANIC BASES

1723. *N*-2-Hydroxyethyldimethylamine (2-Dimethylaminoethanol)
[108-01-0] **$C_4H_{11}NO$**



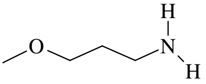
HCS 1980, 422

Cellulose nitrate
See CELLULOSE NITRATE: AMINES

Other reactants
Yoshida, 1980, 167
MRH values calculated for 14 combinations with oxidants are given.
See other ORGANIC BASES

1724. 3-Methoxypropylamine

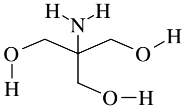
[5332-73-0] **$C_4H_{11}NO$**



Energy of decomposition (in range 150—550°C) measured as 0.57 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AMINOMETHOXY COMPOUNDS

1725. Tris(hydroxymethyl)methylamine

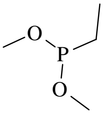
[77-86-1] **$C_4H_{11}NO_3$**



Preparative hazard
See Tris(hydroxymethyl)nitromethane: Hydrogen, etc.
See other ORGANIC BASES

1726. Dimethyl ethanephosphonite

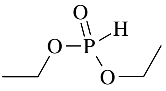
[15715-42-1] **$C_4H_{11}O_2P$**



Arbuzov, B. A. *et al., Chem. Abs.*, 1953, **47**, 3226a
It ignites in air when absorbed onto filter paper.
See other PHOSPHORUS ESTERS, PYROPHORIC MATERIALS

1727. Diethyl phosphite

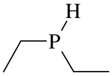
[762-04-9] **$C_4H_{11}O_3P$**



4-Nitrophenol
Phifer, L. H., private comm., 1982
Interaction in absence of solvent in a stirred flask heated by a regulated mantle led to a runaway reaction and explosion.
See other PHOSPHORUS ESTERS

1728. Diethylphosphine

[627-49-6] **$C_4H_{11}P$**



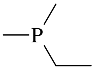
Houben-Weyl 1963, Vol. 12.1, 69

Secondary lower-alkylphosphines readily ignite in air.

See other ALKYLPHOSPHINES

1729. Ethyldimethylphosphine

[1605-51-2] **$C_4H_{11}P$**



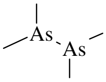
Smith, J. F., private comm., 1970

May ignite in air.

See other ALKYLPHOSPHINES

1730. Tetramethyldiarsane (Tetramethyldiarsine)

[471-35-2] **$C_4H_{12}As_2$**



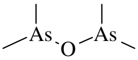
Sidgwick, 1950, 770

Inflames in air.

See other ALKYLNON-METALS

1731. Bis(dimethylarsinyl) oxide

[503-80-0] **$C_4H_{12}As_2O$**



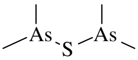
von Schwartz, 1918, 322

Ignites in air.

See related ALKYLNON-METALS

1732. Bis(dimethylarsinyl) sulfide

[591-10-6] **$C_4H_{12}As_2S$**



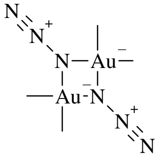
von Schwartz, 1918, 322

Ignites in air.

See related ALKYLNON-METALS

1733. Tetramethyldigold diazide

[22653-19-6] **$C_4H_{12}Au_2N_6$**



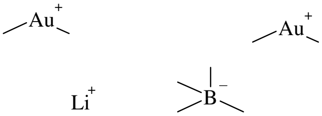
Beck, W. *et al., Inorg. Chim. Acta*, 1968, **2**, 468

The dimeric azide is extremely sensitive and may explode under water if touched.

See other GOLD COMPOUNDS, METAL AZIDES

1734. Lithium tetramethylborate

[2169-38-2] **$C_4H_{12}BLi$**



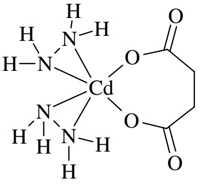
491M, 1975, 238

It may ignite in moist air.

See related ALKYLNON-METALS

1735. Dihydrazinecadmium(II) succinate (Bis(hydrazine)[butanedioato(2—)]cadmium)

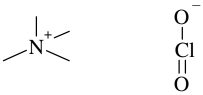
[159793-67-6] **$C_4H_{12}CdN_4O_4$**



See HYDRAZINE METAL MALONATES AND SUCCINATES

1736. Tetramethylammonium chlorite

[67922-18-3] **$C_4H_{12}ClNO_2$**



Levi, *Gazz. Chim. Ital. [1]*, 1922, **52**, 207

The dry solid explodes on impact.
See other CHLORITE SALTS, OXOSALTS OF NITROGENOUS BASES

1737. 1,2-Dichlorotetramethyldisilane

[4342-61-4] **$C_4H_{12}Cl_2Si_2$**

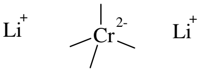
$Me_2ClSiSiClMe_2$

1. Rich J. D., *Chem. Eng. News,* 1990, **68**(13), 2
2. *The Morning Call*, 2000, Sept., 15 & 19
3. Vincent, J. L. *et al., Chem. Eng. News*, 2001, **79**(24), 2

Explosions were experienced in the still-head when distilling this compound. The cause is not very clear and may have to do with impurities [1]. A chemist was injured by an explosion while purifying perhaps 100 g of dichlorotetramethyldisilane, presumably by distillation [2]. A further report of explosions during distillation is presented. The pure compound is said to be thermally stable, but can react violently on heating with sulfuric acid. The standard disilane preparation is likely to leave silyl sulfate related impurities, suspected of being the cause of the problem. Runaway is possible from about 150°C, becoming almost instantaneous at 200°C [3]. This, however, seems more likely to be a pot problem than a still-head one [Ed].
See other ALKYLHALOSILANES

1738. Lithium tetramethylchromate(II)

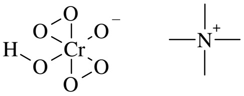
[ ] **$C_4H_{12}CrLi$**



Kurras, E. *et al., J. Organomet. Chem.*, 1965, **4**, 114—118
Isolated as a dioxane complex, it ignites in air.
See other ALKYLMETALS

1739. Tetramethylammonium monoperchromate

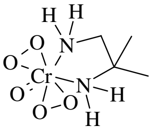
[ ] **$C_4H_{12}CrNO_5$**



Mellor, 1943, Vol 11, 358
It explodes on moderate heating or in contact with sulfuric acid. Now thought probably to have the structure shown (and corresponding empirical formula) it has in the intervening period been considered to be a dimer, a pentaperoxydichromate.
See Tetramethylammonium pentaperoxodichromate
See other OXOSALTS OF NITROGENOUS BASES, PEROXOACID SALTS, PEROXOCHROMIUM COMPOUNDS, QUATERNARY OXIDANTS

1740. 1,2-Diamino-2-methylpropaneoxodiperoxochromium(VI)

[ ] **$C_4H_{12}CrN_2O_5$**



House, D. A. *et al., Inorg. Chem.*, 1967, **6**, 1078 (footnote 6)

This blue precipitate is formed intermediately during preparation of 1,2-diamino-2-methylpropaneaquadiperoxochromium(IV) monohydrate, and its analogues are dangerously explosive and should not be isolated without precautions.

See other AMMINECHROMIUM PEROXOCOMPLEXES

1741. Tetramethylammonium pentafluoroxenoxide

[161535-97-3] **$C_4H_{12}F_5NOXe$**

Christe, K. O. *et al., Inorg. Chem.*, 1995, **34**(7), 1868

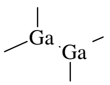
Not surprisingly, this salt is highly explosive.

See also QUATERNARY OXIDANTS

See other XENON COMPOUNDS

1742. Tetramethyldigallane

[65313-37-3] **$C_4H_{12}Ga_2$**



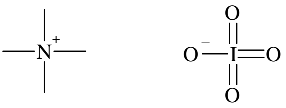
Leleu, *Cahiers*, 1977, (88), 366

It ignites in air.

See other ALKYLMETALS

1743. Tetramethylammonium periodate (*N,N,N*-Trimethylmethaminium periodate)

[55999-69-4] **$C_4H_{12}IO_4$**



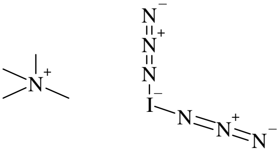
1. Wagner, R. I. *et al., Inorg. Chem.*, 1997, **36**(12), 2564
2. Malpass, J. R. *et al., Chem. Brit.*, 1998, **34**(12), 18
3. Cullis, P. M., Personal communication, 1998

Explodes violently on heating above 240°C [1]. A I4 g sample exploded while being transferred to a cold, empty, unagitated flask via a polythene powder funnel, injuring the worker. The isolated salt was essentially neutral, so excess periodic acid cannot be involved. Subsequent attempts to explode the material deliberately have failed, but it is felt that static electricity may be the cause [2,3].

See other QUATERNARY OXIDANTS

1744a. Tetramethylammonium diazidoiodate(I)

[68574-13-0] **$C_4H_{12}IN_7$**



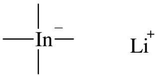
Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 512

Highly explosive crystals.

See related NON-METAL AZIDES

1744b. Lithium tetramethylindate (Lithium indium tetramethyl)

[20740-26-5] **$C_4H_{12}InLi$**



Bradley, D. C. *et al., Inorg. Synth.*, 1997, **31**, 67

It is pyrophoric.

1745. Tetramethylammonium superoxide

[3946-86-9] **$C_4H_{12}NO_2$**

1. McElroy, A. O. *et al., Inorg. Chem.*, 1964, **3**, 1798
2. Foote, C. S., *Photochem. Photobiol.*, 1978, **28**, 718—719

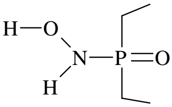
During the preparation by solid phase interaction of tetramethylammonium hydroxide and potassium superoxide [1] by tumbling for several days in a rotary evaporator flask, a violent explosion occurred [2]. This may have been caused by ingress of grease or other organic material leading to contact with potassium superoxide, a powerful oxidant.

See Potassium dioxide: Organic materials

See other QUATERNARY OXIDANTS

1746. *N*-(Diethylphosphinoyl)hydroxylamine

[ ] **$C_4H_{12}NO_2P$**



Harger, M. J. P. *et al., Tetrahedron Lett.*, 1991, **32**(36), 4769

Described as a hazardously unstable oil.

See other N—O COMPOUNDS

1747. Tetramethylammonium ozonate (*N,N,N*-Trimethylmethanaminium ozonide)

[78657-29-1] **$C_4H_{12}NO_3$**

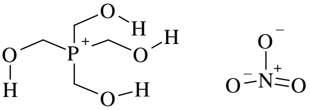
Preparative hazard

See Ozone: Tetramethylammonium hydroxide

See other QUATERNARY OXIDANTS

1748. Tetrakis(hydroxymethyl)phosphonium nitrate

[24748-25-2] **$C_4H_{12}NO_7P$**



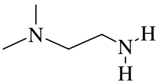
Calamari, T. A. *et al., Chem. Eng. News*, 1979, **57**(12), 74

A violent explosion ocurred during prolonged azeotropic drying at 105—110°C of a 75 wt% benzene solution of the salt. Traces of a nitrate ester may have been formed from a slight excess of nitrate ion.

See related OXOSALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

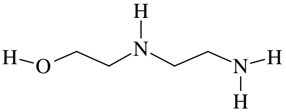
†1749. 2-Dimethylaminoethylamine

[108-00-9] **$C_4H_{12}N_2$**



See other ORGANIC BASES

1750. *N*-2-Hydroxyethyl-1,2-diaminoethane (2-(2-Aminoethyl)aminoethanol)
[111-41-1] **$C_4H_{12}N_2O$**



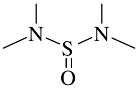
HCS 1980, 555

Cellulose nitrate

See CELLULOSE NITRATE: Amines

See other ORGANIC BASES

1751. Bis(dimethylamino) sulfoxide
[3768-60-3] **$C_4H_{12}N_2OS$**

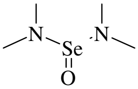


Sulfinyl chloride

See Sulfinyl chloride: Bis(dimethylamino) sulfoxide

See other N—S COMPOUNDS

1752. Seleninyl bis(dimethylamide)
[2424-09-1] **$C_4H_{12}N_2OSe$**

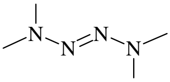


Bailar, 1973, Vol. 2, 975

Vacuum distillation at temperatures around 50—60°C leads to explosive decomposition.

See related *N*-METAL DERIVATIVES, N—S COMPOUNDS

1753. Tetramethyl-2-tetrazene
[6130-87-6] **$C_4H_{12}N_4$**



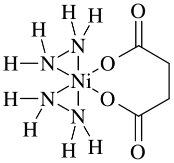
1. Houben-Weyl, 1967, Vol. 10.2, 830
2. Stull, 1977, 22

It explodes above its b.p., 130°C/1 bar [1], and is strongly endothermic (ΔH_f° (l) +226.4 kJ/mol, 1.98 kJ/g) [2].

See other ENDOTHERMIC COMPOUNDS, TETRAZENES

1754. Dihydrazinenickel(II) succinate (Bis(hydrazine)[butanedioato(2—)]nickel)

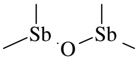
[45101-14-2] **$C_4H_{12}N_4NiO_4$**



See HYDRAZINE METAL MALONATES AND SUCCINATES

1755. Bis(dimethylstibinyl) oxide

[ ] **$C_4H_{12}OSb_2$**



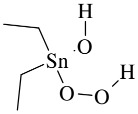
Sidgwick, 1950, 777

It ignites in air.

See related ALKYLMETALS

1757. Diethylhydroxytin hydroperoxide

[ ] **$C_4H_{12}O_3Sn$**



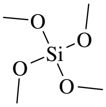
Bailar, 1973, Vol. 2, 68

It is explosive.

See other ORGANOMETALLIC PEROXIDES

†1758a. Tetramethoxysilane (Tetramethyl silicate)

[681-84-5] **$C_4H_{12}O_4Si$**



HCS 1980, 662

Metal hexafluorides

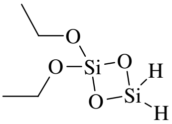
Jacob, E., *Angew. Chem. (Intern. Ed.)*, 1982, **21**, 143, (footnote 6)

During the preparation of the hexamethoxides of rhenium, molybdenum and tungsten by co-condensation with excess tetramethoxysilane on a cold surface, simultaneous co-condensation is necessary to avoid the danger of explosion present when

sequential condensation of the reactants is employed. In the latter case, the high concentration of hexafluoride at the interface leads to violent reaction with the silane.
See related SILANES

1758b. 1,1-Diethoxy-1,3-disiladioxetane

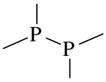
[ ] **$C_4H_{12}O_4Si_2$**



491M, 1975, 150
It ignites in air.
See related NON-METAL HYDRIDES

1759. Tetramethyldiphosphane (Tetramethyldiphosphine)

[3676-91-3] **$C_4H_{12}P_2$**

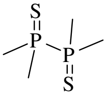


1. Kardosky, G. *et al., Inorg. Synth.*, 1973, **14**, 15
2. Goldsberry, R. *et al., Inorg. Synth.*, 1972, **13**, 28

It ignites in air [1], and unreacted tetramethyldiphosphane residues may also ignite [2].
See Bis(tetramethyldiphosphane disulfide)cadmium perchlorate
See other ALKYLPHOSPHINES

1760. Tetramethyldiphosphane disulfide

[3676-97-9] **$C_4H_{12}P_2S_2$**



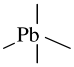
Preparative hazard

1. Parshall. G. W., *Org. Synth.*, 1975, Coll. Vol. 5, 1016
2. Butter, A. S. *et al., Inorg. Synth.*, 1974, **15**, 186
3. Davies, S. G., *Chem. Brit.*, 1984, **20**, 403
4. Bercaw, J. E., *Chem. Eng. News*, 1984, **62**(18), 4
5. Burt, R. J. *et al., J. Organomet. Chem.*, 1979, **182**, 203
6. Bercaw, J. E. *et al., Inorg. Synth.*, 1985, **25**, 199
7. Parshall, G. W., *Org. Synth.*,1985, **63**, 226

The published preparation of the disulfide from thiophosphoryl chloride (4.28 mole) and methylmagnesium iodide (4.0 mole) [1,2] is hazardous. On the stated scale and at the recommended rate of addition of the 47% solution of thiophosphoryl chloride in ether, it

is difficult to maintain the temperature at 0—5°C. Even at below one tenth of the recommended addition rate, after half of the solution had been added during 9 hours, the temperature rose uncontrollably from —5 to +60°C in 10 s and a violent explosion followed, pulverising the apparatus [3]. A closely similar accident was simultaneously reported [4]. An alternative method is recommended [5], the product of which, though air-sensitive, does not ignite in air as previously stated. In the light of experience, the procedure in [1] is preferred to that in [2] because more dilute solutions are used in the former method [6]. To avoid explosions in the preparation of the title compound from methylmagnesium bromide and thiophosphoryl chloride in ether, the chloride should be redistilled and reaction vessel cooling should be with ice—salt rather than acetone—carbon dioxide, to assist in maintaining the reaction temperature in the range 0—5°C. If the temperature drops below —5°C, stop the addition and cautiously warm to 0—5°C [7].
See related ALKYLPHOSPHINES, NON-METAL SULFIDES

1761. Tetramethyllead (Tetramethylplumbane)
[75-74-1] **$C_4H_{12}Pb$**

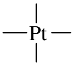


HCS 1980, 895

Sidgwick, 1950, 463
It is liable to explode violently above 90°C.

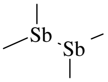
Tetrachlorotrifluoromethylphosphorane
See Tetrachlorotrifluoromethylphosphorane: Tetramethyllead
See other ALKYLMETALS

1762. Tetramethylplatinum
[22295-11-0] **$C_4H_{12}Pt$**



Gilman, H. *et al., J. Amer. Chem. Soc.*, 1953, **75**, 2065
It explodes weakly on heating.
See Trimethylplatinum hydroxide
See other ALKYLMETALS, PLATINUM COMPOUNDS

1763. Tetramethyldistibane (Tetramethyldistibine)
[41422-43-9] **$C_4H_{12}Sb_2$**



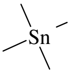
Sidgwick, 1950, 779

It ignites in air.
See other ALKYLMETALS

†1764. Tetramethylsilane
[75-76-3] **$C_4H_{12}Si$**

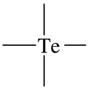
Chlorine
See Chlorine: Antimony trichloride, etc.
See other ALKYLSILANES

†1765. Tetramethyltin (Tetramethylstannane)
[594-27-4] **$C_4H_{12}Sn$**



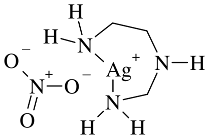
Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Tetramethyltin
See other ALKYLMETALS

1766. Tetramethyltellurium(IV)
[123311-08-0] **$C_4H_{12}Te$**



Gedridge, R. W. *et al., Organometallics*, 1989, **8**(12) 2817
Extremely pyrophoric, sometimes explosively so.
See other ALKYLMETALS

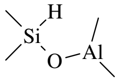
1767. Bis(2-aminoethyl)aminesilver nitrate
[ ] **$C_4H_{13}AgN_4O_3$**



Tennhouse, G. J. *et al., J. Inorg. Nucl. Chem.*, 1966, **28**, 682—684
The complex explodes at 200°C.
See other AMMINEMETAL NITRATES, SILVER COMPOUNDS

1768. 1,1,3,3-Tetramethylsiloxalane

[ ] **$C_4H_{13}AlOSi$**



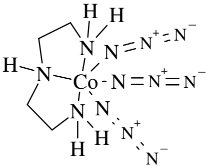
This compound, which exists as the dimer, explodes on contact with water.

See ALKYLALUMINIUM DERIVATIVES

See related ALKYLSILANES

1769. Bis(2-aminoethyl)aminecobalt(III) azide

[26493-63-0] **$C_4H_{13}CoN_{12}$**



Druding, L. F. *et al., Acta Cryst.*, 1974, **B30**, 2386

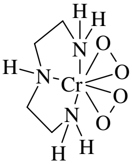
The shock-sensitivity and dangerously explosive nature is stressed.

See AMMINECOBALT(III) AZIDES

See related METAL AZIDES

1770. Bis(2-aminoethyl)aminediperoxochromium(IV)

[59419-71-5] **$C_4H_{13}CrN_3O_4$**

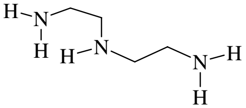


1. House, D. A. *et al., Inorg. Chem.*, 1966, **5**, 840
2. Ghosh, S. K. *et al., J. Organomet. Chem.*, 1988, **340**(1), 59

The monohydrate explodes at 109—110°C during slow heating [1]. The solid complex exploded when manipulated on a glass sinter with a metal spatula [1]. Preparation on small scale and use of plastic equipment is recommended [2].

See other AMMINECHROMIUM PEROXOCOMPLEXES

1771. Bis(2-aminoethyl)amine (Diethylenetriamine)
[111-40-0] **$C_4H_{13}N_3$**



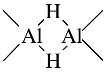
HCS 1980, 399

Cellulose nitrate
See CELLULOSE NITRATE: AMINES

Nitromethane
See Nitromethane: Bis(2-aminoethyl)amine

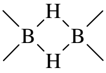
Other reactants
Yoshida, 1980, 147
MRH values calculated for 13 combinations with oxidants are given.
See other ORGANIC BASES

1772. Tetramethyldialuminium dihydride
[33196-65-5] **$C_4H_{14}Al_2$**



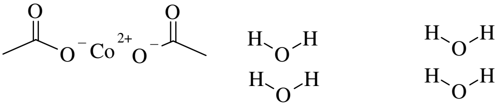
Wiberg, W. E. *et al., Angew. Chem.*, 1939, **52**, 372
It ignites and burns explosively in air.
See other ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

1773. Tetramethyldiborane
[21482-59-7] **$C_4H_{14}B_2$**



Leleu, *Cahiers*, 1977, (88), 365
It ignites in air.
See other ALKYLBORANES

1774. Diacetatotetraaquocobalt (Cobalt(II) acetate tetrahydrate)
[6147-53-1] **$C_4H_{14}CoO_8$**

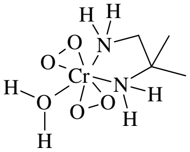


Widmann, G. *et al., Thermochim. Acta*, 1988, **134**, 451—455

Energy of decomposition (270—340°C) was determined by DSC as 2.42 kJ/g, peaking at 328°C. The exotherm is largely from combustion of the evolved carbon monoxide and acetone in air.

See other HEAVY METAL DERIVATIVES, REDUCANTS

1775. 1,2-Diamino-2-methylpropaneaquadiperoxochromium(IV)
[17168-83-1] **$C_4H_{14}CrN_2O_5$**



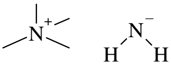
House, D. A. *et al., Inorg. Chem.*, 1967, **6**, 1078

The monohydrate exploded at 83—84°C during slow heating, and is potentially explosive at 20—25°C. There is also a preparative hazard.

See 1,2-Diamino-2-methylpropaneoxodiperoxochromium(VI)

See other AMMINECHROMIUM PEROXOCOMPLEXES

1776. Tetramethylammonium amide
[13422-81-6] **$C_4H_{14}N_2$**



Ammonia

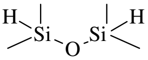
Musker, W. K., *J. Org. Chem.*, 1967, **32**, 3189

During the preparation, the liquid ammonia used as solvent must be removed completely at —45°C. The compound decomposes explosively at ambient temperature in presence of ammonia.

See Sodium: Ammonia, Aromatic hydrocarbons

See related *N*-METAL DERIVATIVES

1777. Tetramethyldisiloxane
[3277-26-7] **$C_4H_{14}OSi_2$**



Allylphenols, Platinum

See SILANES: Olefins, Platinum

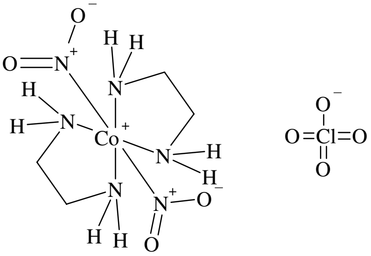
Oxygen, Sodium hydroxide, Water

See Oxygen (Gas): Tetramethyldisiloxane

See related ALKYLSILANES

1778. Bis(1,2-diaminoethane)dinitrocobalt(III) perchlorate

[14781-32-9] (c-) [14781-33-0] (t-) $C_4H_{16}ClCoN_6O_8$



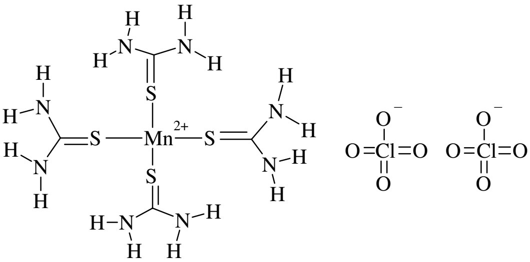
Seel, F. *et al., Z. Anorg. Chem.*, 1974, **408**, 281

The *cis*- and *trans*-isomers are both dangerously explosive compounds.

See other AMMINEMETAL OXOSALTS

1779. Tetrakis(thiourea)manganese(II) perchlorate

[50831-29-3] $\mathbf{C_4H_{16}Cl_2MnN_8O_8S_4}$



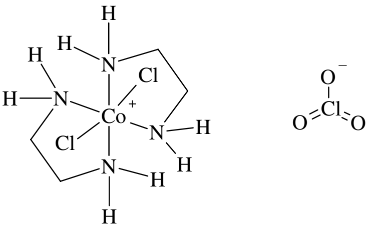
Karnaukhov, A. S. *et al., Chem. Abs.*, 1973, **79**, 140195

The complex decomposes explosively at 257°C.

See related AMMINEMETAL OXOSALTS

1780. Bis(1,2-diaminoethane)dichlorocobalt(III) chlorate

[26388-78-3] $\mathbf{C_4H_{16}Cl_3CoN_4O_3}$

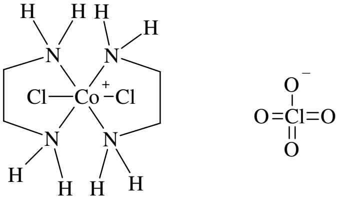


It explodes at 320°C.

See entry AMMINEMETAL OXOSALTS (reference 2)

1781. Bis(1,2-diaminoethane)dichlorocobalt(III) perchlorate

[14932-06-0] **$C_4H_{16}Cl_3CoN_4O_4$**

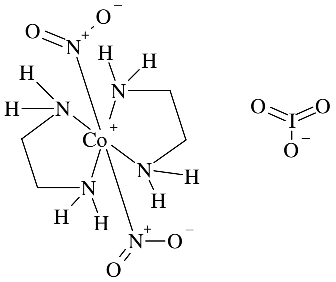


It explodes at 300°C; low impact-sensitivity.

See entry AMMINEMETAL OXOSALTS (reference 2)

1782. *cis*-Bis(1,2-diaminoethane)dinitrocobalt(III) iodate

[ ] **$C_4H_{16}CoIN_6O_7$**



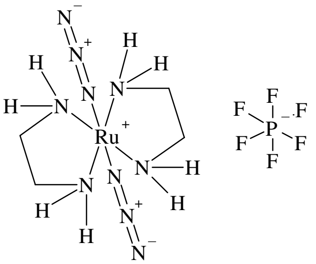
Lobanov, N. I., *Zh. Neorg. Khim.*, 1959, **4**, 151

It dissociates explosively on heating.

See other AMMINEMETAL OXOSALTS

1783. Diazido-bis(1,2-diaminoethane)ruthenium(II) hexafluorophosphate

[30459-28-0] **$C_4H_{16}F_6N_{10}PRu$**

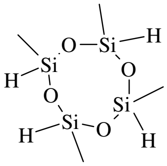


Kane-Maguire, L. A. P. *et al., Inorg. Synth.*, 1970, **12**, 24

Small explosions were observed on scratching the crystals with a metal spatula.

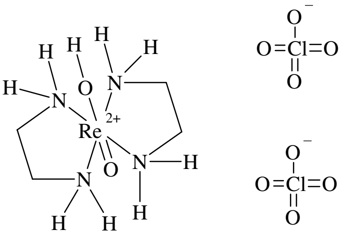
See related METAL AZIDES

1784. 2,4,6,8-Tetramethylcyclotetrasiloxane
[2370-88-9] **$C_4H_{16}O_4Si_4$**



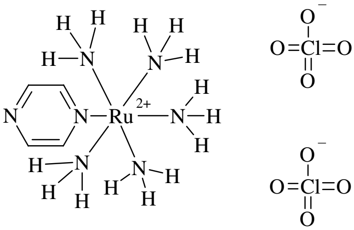
See 2,4,6,8-Tetraethenyl-2,4,6,8-tetramethylcyclotetrasiloxane
See other SILANES

1785. Bis(1,2-diaminoethane)hydroxooxorhenium(V) perchlorate
[19267-68-6] **$C_4H_{17}Cl_2N_4O_{10}Re$**



Murmann, R. K. *et al., Inorg. Synth.*, 1966, **8**, 174—175
It explodes violently when dried at above ambient temperature and is also shock-sensitive. Several explosions occurred during analytical combustion.
See other AMMINEMETAL OXOSALTS

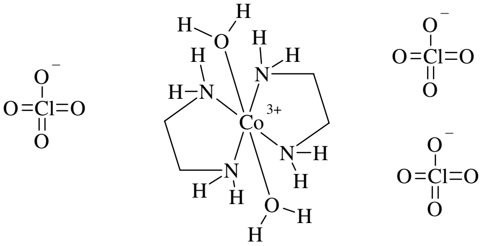
1786. Pentaamminepyrazineruthenium(II) perchlorate
[41481-90-7] **$C_4H_{19}Cl_2N_7O_8Ru$**



Creutz, C. A., private comm., 1969
After ether washing, 30 mg of the salt exploded violently when disturbed.
See other AMMINEMETAL OXOSALTS

1787. Bis(1,2-diaminoethane)diaquacobalt(III) perchlorate

[55870-36-5] **$C_4H_{20}Cl_3CoN_4O_{14}$**



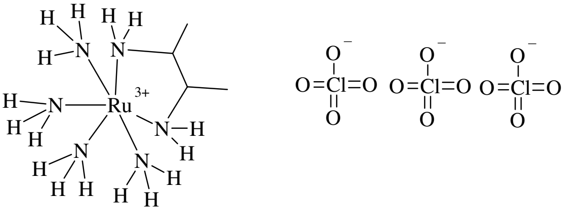
Seel, F. *et al., Z. Anorg. Chem.*, 1974, **408**, 281

During evaporation of a solution of the complex salt, a very violent explosion occurred.

See other AMMINEMETAL OXOSALTS

1788. Tetraammine-2,3-butanediimineruthenium(III) perchlorate

[56370-81-1] **$C_4H_{20}Cl_3N_6O_{12}Ru$**



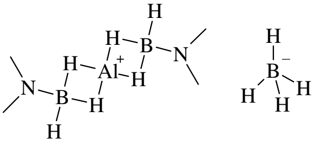
Evans, I. P. *et al., J. Amer. Chem. Soc.*, 1977, **98**, 8042

It is explosive.

See other AMMINEMETAL OXOSALTS

1789. Bis(dimethylaminoborane)aluminium tetrahydroborate

[39047-21-7] **$C_4H_{22}AlB_3N_2$**



Air, or Water

Burg, A. B. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 957

The impure oily product ignites in air and reacts violently with water.

See other COMPLEX HYDRIDES

See related BORANES

1790. 1,1-′Azo-1,2-dicarbadodecaborane(14)

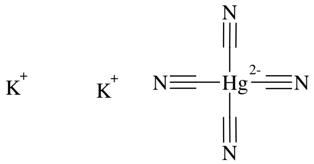
[ ] **$C_4H_{22}B_{20}N_2$**

[1388]

See entry AZOCARBABORANES

1791. Potassium tetracyanomercurate(II)

[591-89-9] **$C_4HgK_2N_4$**



Ammonia

Pieters, 1957, 30

Contact may be explosive.

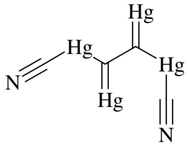
See Potassium hexacyanoferrate(III): Ammonia

See other MERCURY COMPOUNDS

See related METAL CYANIDES

1792. *μ*-1,2-Bis(cyanomercurio)ethanediylidenedimercury(II)

[ ] **$C_4Hg_4N_2$**



Whitmore, 1921, 128

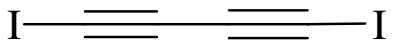
It explodes slightly on heating.

See other MERCURY COMPOUNDS

See related METAL CYANIDES

1793. 1,4-Diiodo-1,3-butadiyne

[53214-97-4] **C_4I_2**



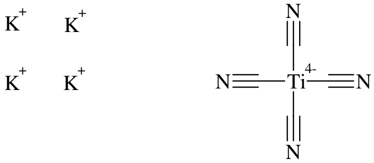
Sorbe, 1968, 66

It explodes at about 100°C.

See other HALOACETYLENE DERIVATIVES

1794. Potassium tetracyanotitanate(IV)

[75038-71-0] **$C_4K_4N_4Ti$**



Water

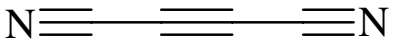
Nicholls, D. *et al., J. Chem. Soc., Chem Comm.*, 1974, 635—636

Interaction is violent.

See other METAL CYANIDES

†1795. Dicyanoacetylene (2-Butynedinitrile)

[1071-98-3] **C_4N_2**



1. Kirshenbaum, A. D. *et al., J. Amer. Chem. Soc.*, 1956, **78**, 2020
2. Robinson-Rodd, 1965, Vol. ID, 338, 366
3. Ciganek, E. *et al., J. Org. Chem.*, 1968, **33**, 542

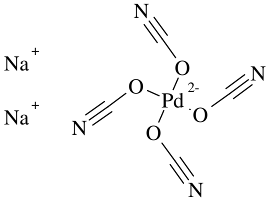
As anticipated for a conjugated multiple triply bound structure, it is extremely endothermic (ΔH_f° (g) +626.4 kJ/mol, 8.22 kJ/g), and may decompose explosively to carbon powder and nitrogen. When burnt in oxygen a flame temperature exceeding 4700°C is attained [1], and it ignites in air at 130°C [2]. It is potentially explosive in the pure state or in conc. solutions, but is fairly stable in dilute solution [3]. It rapidly polymerises with water, weak bases, alcohols, etc. [2].

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

See related HALOACETYLENE DERIVATIVES

1796. Sodium tetracyanatopalladate(II)

[ ] **$C_4N_4Na_2O_4Pd$**



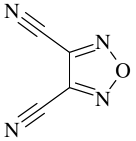
Bailar, 1973, Vol. 3, 1288

It explodes on heating or impact.

See related METAL CYANATES

1797. Dicyanofurazan

[55644-07-0] **C_4N_4O**



Homewood, R. H. *et al.*, US Pat. 3 832 249, 1974

Although highly endothermic (ΔH_f° (s) +456.3 kJ/mol, 3.80 kJ/g), it is a stable and relatively insensitive but powerful explosive.

Nitrogenous bases

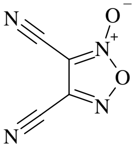
Denson, D. B. *et al.*, US Pat. 3 740 947, 1973

Contact of dicyanofurazan, or its *N*-oxide (dicyanofuroxan), with hydrazine, mono- or di-methylhydrazine, piperidine, piperazine, diethylamine or their mixtures is instantaneously explosive.

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, N—O COMPOUNDS

1798. Dicyanofurazan *N*-oxide (Dicyanofuroxan)

[55644-07-0] **$C_4N_4O_2$**



It is highly endothermic (ΔH_f° (s) +565.5 kJ/mol, 3.43 kJ/g).

Nitrogenous bases

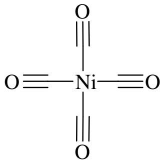
Denson, D. B. *et al.*, US Pat. 3 740 947, 1973

Contact of dicyanofurazan *N*-oxide or the parent furazan with hydrazine, mono- or di-methylhydrazine, piperidine, piperazine, diethylamine or their mixtures is instantaneously explosive.

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, FURAZAN *N*-OXIDES

†1799. Tetracarbonylnickel (Nickel tetracarbonyl)

[13463-39-3] **C_4NiO_4**



HCS 1980, 885

Bromine

Blanchard, A. A. *et al., J. Amer. Chem. Soc.*, 1926, **48**, 872

The two compounds interact explosively in the liquid state, but smoothly as vapour.

Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Tetracarbonylnickel

Mercury, Oxygen

Mellor, 1946, Vol. 5, 955

A mixture of the dry carbonyl and oxygen will explode on vigorous shaking with mercury (presumably catalysed by mercury or its oxide).

Oxygen, Butane

1. Egerton, A. *et al., Proc. R. Soc.*, 1954, **A225**, 427
2. Badin, E. J. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 2055

The carbonyl on exposure to atmospheric oxygen produces a deposit which becomes peroxidised and may ignite. Mixtures with air or oxygen at low partial and total pressures explode after a variable induction period [1]. Addition of the carbonyl to a butane—oxygen mixture at 20—40°C caused explosive reaction in some cases [2].

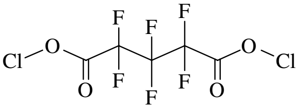
See other INDUCTION PERIOD INCIDENTS

Tetrachloropropadiene

See Dicarbonyl-η-trichloropropenyldinickel chloride dimer

See other CARBONYLMETALS

1800. Hexafluoroglutaryl dihypochlorite
[71359-64-3] **$C_5Cl_2F_6O_4$**

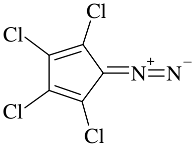


Tari, I. *et al.*, *Inorg. Chem.*, 1979, **18**, 3205—3208

Explosive above —10°C.

See other ACYL HYPOHALITES

1801. Tetrachlorodiazocyclopentadiene
[21572-61-2] **$C_5Cl_4N_2$**

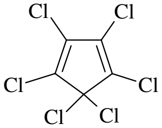


Abel, E. W. *et al., Inorg. Chim. Acta*, 1980, **44**(3), L161—163

Conversion to octachloronaphthalene by heating at 150°C in absence of solvent was explosive.
See other DIAZO COMPOUNDS

1802. Hexachlorocyclopentadiene

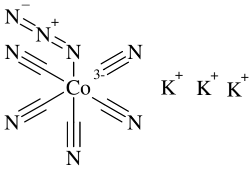
[77-47-4] **C_5Cl_6**



Sodium
See Sodium: Halocarbons
See other HALOALKENES

1803. Potassium azidopentacyanocobaltate(3—)

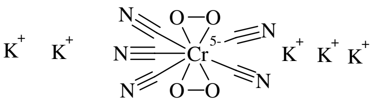
[14705-99-8] **$C_5CoK_3N_8$**



Huan, J. *et al., Thermochim. Acta*, 1988, **130**, 77—85
Thermal decomposition under hydrogen of a series of pentacyanocobaltate complexes (CN-, NO_2-, NO- or N_3- ligands) revealed that the latter complex is the most exothermic by far. Presence of iron powder suppresses hydrogen cyanide formation.
See related METAL AZIDES, METAL CYANIDES(AND CYANO COMPLEXES)

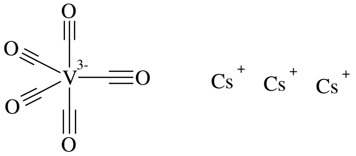
1804. Potassium pentacyanodiperoxochromate(5—)

[ ] **$C_5CrK_5N_5O_4$**



Bailar, 1973, Vol. 4, 167
A highly explosive material, with internal redox features.
See other REDOX COMPOUNDS
See related AMMINECHROMIUM PEROXOCOMPLEXES

1805. Caesium pentacarbonylvanadate(3—)
[78937-12-9] **$C_5Cs_3O_5V$**



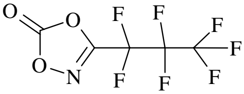
Air, or Hydroxy compounds

Ellis, J. F. *et al., J. Amer. Chem. Soc.*, 1981, **103**, 6101

Pyrophoric in air, deflagrates under nitrogen on scratching with a metal spatula, and reacts explosively with alcohols or water.

See related CARBONYLMETALS

1806. 2-Heptafluoropropyl-1,3,4-dioxazolone
[87050-95-1] **$C_5F_7NO_3$**



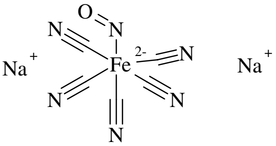
Middleton, W. J., *J. Org. Chem.*, 1983, **48**, 3845

It could not be detonated by hot wire initiation, but a sample exploded during distillation at ambient pressure at 102°C.

See 1,3,4-DIOXAZOLONES

See other N—O COMPOUNDS

1807. Sodium pentacyanonitrosylferrate(2—)
[14402-89-2] **$C_5FeN_6Na_2O$**

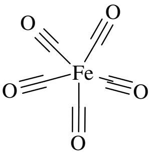


Sodium nitrite

See Sodium nitrite: Metal cyanides

See related METAL CYANIDES

†1808a. Pentacarbonyliron (Iron pentacarbonyl)
[13463-40-6] **C_5FeO_5**



Merck, 1983, 736
Pyrophoric in air.

Acetic acid, Water

Braye, E. H. *et al., Inorg. Synth.*, 1966, **8**, 179

A brown pyrophoric powder is produced if the carbonyl is dissolved in acetic acid containing above 5% of water.

Nitrogen oxide

See Nitrogen oxide: Pentacarbonyliron

Pentaborane(9), Pyrex glass

See Pentaborane(9): Pentacarbonyliron, etc.

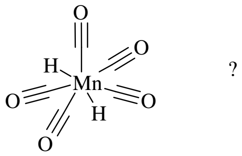
Transition metal halides, Zinc

Lawrenson, M. J., private comm., 1970

The preparation of carbonylmetals by treating a transition metal halide either with carbon monoxide and zinc, or with iron pentacarbonyl is well-known and smooth. However, a violent eruptive reaction occurs if a methanolic solution of a cobalt halide, a rhodium halide or a ruthenium halide is treated with both zinc and iron pentacarbonyl.

See other CARBONYLMETALS

1808b. Pentacarbonylmanganese hydride $C_5H_2MnO_5$

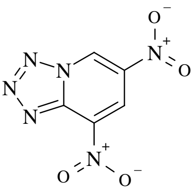


Usher J., www.dne.bnl.gov/etd/csc/1993, 1993 (quarter 2)

An explosion of 1 gm of a hydride thus named, but without more definite identification , during storage in a refrigerator is reported. Such a species might very well evolve either carbon monoxide, or hydrogen, in storage, pressurising its container.

See other CARBONYLMETALS, METAL HYDRIDES

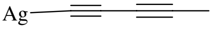
1808c. 4,6-Dinitrotetrazolo[1,5-a]pyridine (6,8-Dinitrotetrazolo[1,5-*a*]pyridine) [127183-60-2] $C_5H_2N_6O_4$



Boubaker, T. *et al., Org & Biomolecular Chem.*, 2003, **1**(15), 2764

Reaction with nucleophiles, in particular potassium hydroxide and methoxide, forms Meisenheimer adducts similar to those of dinitrobenzofurazan *N*-oxide, in both structure and explosivity, but even more readily.
See 4,6-Dinitrobenzofurazan *N*-oxide

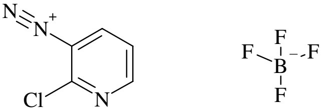
1809. 1,3-Pentadiyn-1-ylsilver
[ ] **C_5H_3Ag**



Alone, or Sulfuric acid

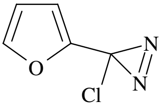
Schluhbach, H. H. *et al., Ann.*, 1950, **568**, 155
Very sensitive to impact or friction, and explodes when moistened with sulfuric acid.
See other METAL ACETYLIDES, SILVER COMPOUNDS

1810. 2-Chloro-3-pyridinediazonium tetrafluoroborate
[70682-07-4] **$C_5H_3BClF_4N_3$**



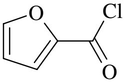
Verde, C., Span. Pat. ES 548 695, 1986
The diazonium salt decomposes violently above 25°C or when dry.
See other DIAZONIUM TETRAHALOBORATES

1811. 2-Furylchlorodiazirine (3-Chloro,3-(2-furanyl)diazirine)
[201533-16-6] **$C_5H_3ClN_2$**



Khasanova, T. *et al., J. Amer. Chem. Soc.*, 1998, **120**(1), 233
This previously unknown compound is, not surprisingly, detonable.
See other DIAZIRINES

1812. Furoyl chloride
[1300-32-9] **$C_5H_3ClO_2$**



Preparative hazard

Wrigley, T. C., private comm., 1979

A sample of freshly distilled material exploded violently during overnight storage. Self-acylation or polymerisation catalysed by hydrogen chloride may have been involved.

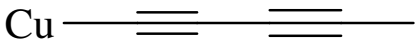
See Phosphorus trichloride: Carboxylic acids

See also 2-HALOMETHYL-FURANS OR -THIOPHENES

See other ACYL HALIDES, POLYCONDENSATION REACTION INCIDENTS

1813. 1,3-Pentadiyn-1-ylcopper

[115609-87-5] **C_5H_3Cu**



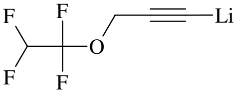
Schluhbach, H. H. *et al., Ann.*, 1950, **568**, 155

Explodes on impact or friction.

See other METAL ACETYLIDES

1814. Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide

[82906-06-7] **$C_5H_3F_4LiO$**



Von Werner, K., *J. Fluorine Chem.*, 1982, **20**, 215—216

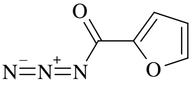
The explosion during work-up of a substantial amount of the lithiated fluorocompound emphasises the need for great care and full precautions in handling such materials.

See other METAL ACETYLIDES

See related HALOACETYLENE DERIVATIVES

1815. 2-Furoyl azide

[20762-98-5] **$C_5H_3N_3O_2$**



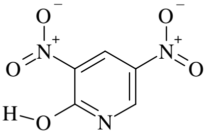
Dunlop, 1953, 544

The azide explodes violently on heating in absence of a solvent or diluent.

See other ACYL AZIDES

1816. 2-Hydroxy-3,5-dinitropyridine

[2980-33-8] **$C_5H_3N_3O_5$**



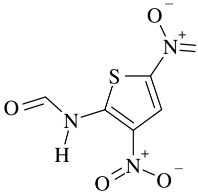
Glowiak, B., *Chem. Abs.*, 1963, **58**, 498h

Various heavy metal salts show explosive properties, and the lead salt might be useful as an initiating explosive.

See other POLYNITROARYL COMPOUNDS

1817. 2-Formylamino-3,5-dinitrothiophene

[ ] **$C_5H_3N_3O_5S$**



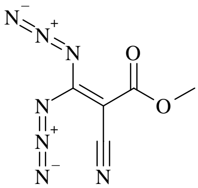
Fast flame propagation on heating the powder moderately.

See entry HIGH RATE DECOMPOSITION

See other POLYNITROARYL COMPOUNDS

1818. Methyl 3,3-diazido-2-cyanoacrylate

[82140-87-2] **$C_5H_3N_7O_2$**



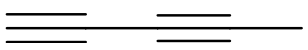
Saalfrank, R. W. *et al., Angew. Chem. (Intern. Ed.)*, 1987, **26**, 1161 (footnote 14)

The crystalline solid decomposes explosively around 70°C, so working scale was limited to 0.5 g.

See other CYANO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

1819. 1,3-Pentadiyne

[4911-55-1] **C_5H_4**



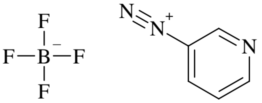
Brandsma, 1971, 7, 36

It explodes on distillation at ambient pressure.

See other ACETYLENIC COMPOUNDS

1820. 3-Pyridinediazonium tetrafluoroborate

[586-92-5] **$C_5H_4BF_4N_3$**



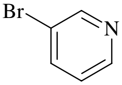
1. Johnson, E. P. *et al., Chem. Eng. News*, 1967, **45**(44), 44
2. Roe, A. *et al., J. Amer. Chem. Soc.*, 1947, **69**, 2443

A sample, air-dried on aluminium foil, exploded spontaneously and another sample exploded on heating to 47°C [1]. The earlier reference describes the instability of the salt above 15°C if freed from solvent, and both the 2- and 4-isomeric salts were found to be very unstable and incapable of isolation [2].

See other DIAZONIUM TETRAHALOBORATES

1821. 3-Bromopyridine

[626-55-1] **C_5H_4BrN**

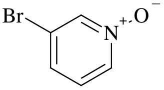


Acetic acid, Hydrogen peroxide

See Hydrogen peroxide: Acetic acid, *N*-Heterocycles

1822. 3-Bromopyridine *N*-oxide

[2402-97-3] **C_5H_4BrNO**

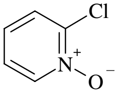


Preparative hazard

See Hydrogen peroxide: Acetic acid, *N*-Heterocycles

1823. 2-Chloropyridine *N*-oxide

[2402-95-1] **C_5H_4ClNO**

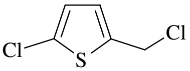


1. Kotoyori, T., private comm., 1983
2. *MARS Database*, 1998, short report, accident 025

A 500 kg batch had been prepared in glacial acetic acid using 35% aqueous hydrogen peroxide with 2% sulfuric acid as catalyst. When the reaction was complete, solvents were removed by vacuum distillation, steam was turned off and the reaction vessel

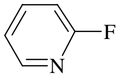
jacket filled with water. After standing overnight, violent decomposition of the contents occurred, causing the safety valve to lift, even although the vessel was vented via its condenser/receiver system. An external fire ensued, and carbonised residue was found inside the reactor. It was surmised that as the product began to solidify inwards from the outer cooled reactor wall, the inner liquid material effectively went into adiabatic storage. The compound is of limited thermal stability and begins to decompose exothermally at 90—100°C, and salt formation from liberated hydrogen chloride will tend to accelerate the process. The hot weather (and possibly a leak of steam into the jacket) may have exaggerated the adiabatic effect. The necessity to assess thermal stabilities of reactants and products, to minimise heating times and to maximise cooling rates, and to monitor and supervise processes is stressed [1]. Another report of a process explosion during manufacture of this, using maleic anhydride as catalyst and without a solvent, was attributed to adding a shot of 70% hydrogen peroxide slightly faster than normal. Since the reaction was almost complete and no product remained in the reactor afterwards, it is possible that the amine oxide was also implicated [2].
See other *N*-OXIDES

1824. 2-Chloro-5-chloromethylthiophene
[23784-96-5] **$C_5H_4Cl_2S$**



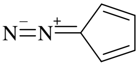
Rosenthal, N. A., *J. Amer. Chem. Soc.*, 1951, **73**, 590
Storage at ambient temperature may lead to explosively violent decomposition.
See other 2-HALOMETHYL-FURANS OR -THIOPHENES

1825. 2-Fluoropyridine
[372-48-5] **C_5H_4FN**



Bromine trifluoride
See Bromine trifluoride: Pyridine

1826. Diazocyclopentadiene
[1192-27-4] **$C_5H_4N_2$**



1. Ramirez, F., *J. Org. Chem.*, 1958, **23**, 2036—2037
2. Wedd, A. G., *Chem. & Ind.*, 1970, 109
3. Aarons, L. J. *et al., J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1108
4. DeMore, W. B. *et al., J. Amer. Chem. Soc.*, 1959, **81**, 5875

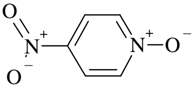
5. Weil, T., *J. Org. Chem.*, 1963, **28**, 2472
6. Regitz, M. *et al., Tetrahedron*, 1967, **23**, 2706
7. Gillespie, R. J. *et al., J. Chem. Soc., Perkin Trans. 1*, 1979, 2626
8. Reimer, K. J. *et al., Inorg. Synth.*, 1980, **20**, 189

A violent explosion occurred after distillation at 47—49°C/60—65 mbar [1] and also during distillation at 48—53°C/66 mbar; use of solutions of undistilled material was recommended [2]. The compound exploded on one occasion in the solid state after condensation at —196°C, probably owing to fortuitous tribomechanical shock [3]. A similar explosion on chilling a sample in liquid nitrogen had been noted previously [4]. Of two simplified methods of isolating the material without distillation [4,5], the former appears to give higher yields. A further explosion during distillation has been reported [7], but solutions in pentane are considered convenient and safe [8].

See other DIAZO COMPOUNDS

1827. 4-Nitropyridine *N*-oxide

[1124-33-0] **$C_5H_4N_2O_3$**



Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate

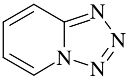
Kurbatova, A. S. *et al., Chem. Abs.*, 1978, **88**, 120946

Dehydrogenation of the ‘Hantzsch’ ester in a melt with the oxide at 130—140°C proceeded explosively.

See other *N*-OXIDES

1828. 1,2-Dihydropyrido[2,1-*e*]tetrazole

[ ] **$C_5H_4N_4$**



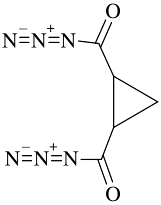
Fargher, R. G. *et al., J. Chem. Soc.*, 1915, **107**, 695

Explodes on touching with a hot rod.

See other TETRAZOLES

1829. 1,2-Bis(azidocarbonyl)cyclopropane

[68979-48-6; 114752-52-2] (cis, trans, resp.) **$C_5H_4N_6O_2$**



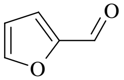
1. Landgrebe, J. A., *Chem. Eng. News*, 1981, **59**(17), 47
2. Majchrzak, M. W. *et al., Synth. Comm.*, 1981, **11**, 493—495
3. Johnson, R. E., *Chem. Eng. News*, 1988, **66**(13), 2

Trituration of the crude *cis*-azide with hexane at ambient temperature caused detonation to occur. Isolation of low molecular weight carbonyl azides should be avoided, or extreme precautions taken. A similar incident with the analogous cyclobutane diazide was reported [1]. During use as an intermediate in preparation of the 1,2-diamine, the explosive diazide was never isolated or handled free of solvent [2]. The *trans* isomer (0.25 mole) was prepared by the latter technique, but as a 45 w/v% solution in toluene, rather than as the recommended 10% solution. When a magnetic spin-bar was introduced, the solution detonated. Initiation may have involved friction from adventitious presence of iron filings adhering to the magnetic bar [3].

See other ACYL AZIDES, FRICTIONAL INITIATION INCIDENTS

1830. 2-Furaldehyde (Furfural)

[98-01-1] **$C_5H_4O_2$**



HCS 1980, 511

Other reactants

Yoshida, 1980, 313

MRH values calculated for 13 combinations with oxidants are given.

Sodium hydrogen carbonate

Unpublished information, 1977

Several cases of spontaneous ignition after exposure to air of fine coke particles removed from filter strainers on a petroleum refinery furfural extraction unit have been noted. This has been associated with the use of sodium hydrogen carbonate (bicarbonate) injected into the plant for pH control, which produced a pH of 10.5 locally. This would tend to resinify the aldehyde, but there is also the possibility of a Cannizzaro reaction causing conversion of the aldehyde to furfuryl alcohol and furoic acid. The latter, together with other acidic products of autoxidation of the aldehyde, would tend to resinify the furfuryl alcohol. Pyrolysis GLC showed the presence of a significant proportion of furfuryl alcohol-derived resins in the coke. The latter is now discarded into drums of water, immediately after discharge from the strainers, to prevent further incidents.

See Furfuryl alcohol: Acids

See other PYROPHORIC MATERIALS

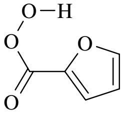
Sodium hypochlorite

See Sodium hypochlorite: Furfuraldehyde

See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

1831. Peroxyfuroic acid

[5797-06-8] **$C_5H_4O_4$**



Alone, or Metal salts, or Organic materials

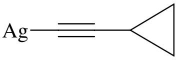
Milas, N. A. *et al., J. Amer. Chem. Soc.*, 1934, **56**, 1221

Thermal decomposition of the acid becomes violently explosive at 40°C. Intimate contact with finely divided metal salts (mainly halides), ergosterol, pyrogallol or animal charcoal led to explosive decomposition (often violent) in 18 out of 28 experiments.

See other PEROXYACIDS

1832. Silver cyclopropylacetylide

[ ] **C_5H_5Ag**



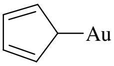
Slobodin, Ya. M. *et al., Chem. Abs.*, 1952, **46**, 10112e

It explodes on heating.

See other METAL ACETYLIDES, SILVER COMPOUNDS

1833. Cyclopentadienylgold(I)

[21254-73-9] **C_5H_5Au**



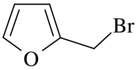
Huttel, R. *et al., Angew. Chem. (Intern. Ed.)*, 1967, **6**, 862

It is sensitive to friction and heat, often deflagrating on gentle warming.

See other ALKYLMETALS, GOLD COMPOUNDS

1834. 2-Bromomethylfuran

[4437-18-7] **C_5H_5BrO**

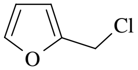


Dunlop, 1953, 231

It is very unstable, and the liberated hydrogen bromide accelerates further decomposition to explosive violence.

See other 2-HALOMETHYL-FURANS OR -THIOPHENES

1835. 2-Chloromethylfuran
[617-88-9] **C_5H_5ClO**

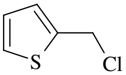


Anon., *ABCM Quart. Safety Summ.*, 1962, **33**, 2

A small sample of freshly prepared and distilled material, when stored over a weekend, exploded violently owing to polymerisation or decomposition (probably arising from the facile hydrolysis with traces of moisture and liberation of hydrogen chloride). Material should be prepared and used immediately, but if brief storage is inevitable, refrigeration is essential.

See other 2-HALOMETHYL-FURANS OR -THIOPHENES

1836. 2-Chloromethylthiophene
[617-88-9] **C_5H_5ClS**



1. Bergeim, F. H., *Chem. Eng. News*, 1952, **30**, 2546
2. Meyer, F. C., *Chem. Eng. News*, 1952, **30**, 3352
3. Wiberg, K. B., *Org. Synth.*, 1955, Coll. Vol. 3, 197

The material is unstable and gradually decomposes, even when kept cold and dark, with liberation of hydrogen chloride which accelerates the decomposition [1]. If kept in closed containers, the pressure increase may cause an explosion [2]. Amines stabilise the material, which may then be kept cold in a vented container for several months [3].

See other GAS EVOLUTION INCIDENTS, 2-HALOMETHYL-FURANS OR -THIOPHENES

1837. Poly(cyclopentadienyltitanium dichloride)
[35398-20-0] **$(C_5H_5Cl_2Ti)_n$**

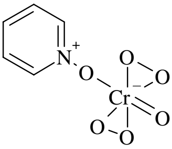
[1431]

Lucas, C. R. *et al., Inorg, Synth.*, 1976, **16**, 238

It is pyrophoric in air.

See other ORGANOMETALLICS, PYROPHORIC MATERIALS

1838. Oxodiperoxopyridinechromium *N*-oxide
[38293-27-5] **$C_5H_5CrNO_6$**



1. Westland, A. D. *et al., Inorg. Chem.*, 1980, **19**, 2257
2. Daire, E. *et al., Nouv. J. Chim.*, 1984, **8**, 271—274

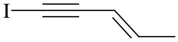
This chromium complex, and the molybdenum and tungsten analogues with two *N*-oxide ligands, were all explosive [1]. The chromium complex has exploded during desiccation [2].

See Triphenylphosphine oxide-oxodiperoxochromium(VI)

See other AMMINECHROMIUM PEROXOCOMPLEXES

1839. 1-Iodo-3-penten-1-yne

[ ] **C_5H_5I**



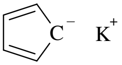
Vaughn, J. A. *et al., J. Amer. Chem. Soc.*, 1934, **56**, 1208

After distillation at 72°C/62 mbar, the residue always exploded if heating were continued.

See other HALOACETYLENE DERIVATIVES

1840. Potassium cyclopentadienide

[30994-24-2] **C_5H_5K**



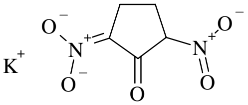
Angus, P. L. *et al., Inorg. Synth.*, 1977, **17**, 177

The dry powder is very air-sensitive and pyrophoric.

See other ALKYLMETALS, PYROPHORIC MATERIALS

1841. Potassium 2,5-dinitrocyclopentanonide

[26717-79-3] **$C_5H_5KN_2O_5$**



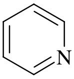
Wieland, H. *et al., Ann.*, 1928, **461**, 304

The salt (possibly an *aci*-nitro salt) explodes at 154—158°C and is less stable than the di-potassium salt (241—245°C).

See other C—NITRO COMPOUNDS

†1842. Pyridine

[110-86-1] **C_5H_5N**



NSC 310, 1978; *FPA H58*, 1977; *HCS 1980*, 802; *RSC Lab. Hazard Data Sheet No. 8*, 1983

Moderately endothermic: ΔH_f° (l) 100 kJ/mole, 1.3 kJ/g
See other ENDOTHERMIC COMPOUNDS

Formamide, Iodine, Sulfur trioxide
See Formamide: Iodine, etc.

Maleic anhydride
See Maleic anhydride: Bases, etc.

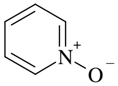
Other reactants
Yoshida, 1980, 292
MRH values calculated for 15 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Bromine trifluoride: Pyridine	MRH 3.05/75
Chromium trioxide: Pyridine	MRH 3.05/75
Dinitrogen tetraoxide: Heterocyclic bases	MRH 7.07/78
Fluorine: Nitrogenous bases	
Trifluoromethyl hypofluorite: Pyridine	

See other ORGANIC BASES

1843. Pyridine *N*-oxide

[694-59-7] **C_5H_5NO**



Energy of decomposition (in range 250—380°C) measured as 1.076 kJ/g by DSC, and T_{ait24} was determined as 205°C by adiabatic Dewar tests, with an apparent energy of activation of 124 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Hexamethyldisilane, Tetrabutylammonium fluoride
Vorbrueggen, H. *et al., Tetrahedron Lett.*, 1983, **24**, 5337
Slow addition of hexamethyldisilane in THF to pyridine *N*-oxide and tetrabutylammonium fluoride in THF effected smooth reduction to pyridine, while addition of undiluted fluoride led to an explosion on two occasions.
See other *N*-OXIDES

1844. Methylnitrothiophene

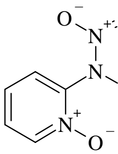
[ ] **$C_5H_5NO_2S$**

Preparative hazard

See Nitric acid: Methylthiophene

See other C-NITRO COMPOUNDS

1845. 2-(*N*-Nitroamino)pyridine *N*-oxide
[85060-25-9] **$C_5H_5N_3O_3$**

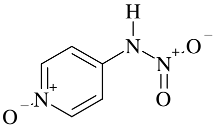


Talik, T. *et al., Chem. Abs.*, 1983, **98**, 160554

Powerfully explosive.

See other N—NITRO COMPOUNDS, N-OXIDES

1846. 4-(*N*-Nitroamino)pyridine N-oxide (*N*-Nitro-4-pyridinamine 1-oxide)
[85060-27-1] **$C_5H_5N_3O_3$**

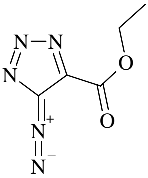


Talik, T. *et al., Chem. Abs.*, 1983, **98**, 160554

Powerfully explosive.

See other N—NITRO COMPOUNDS, N-OXIDES

1847. Ethyl 4-diazo-1,2,3-triazole-5-carboxylate
[85807-69-8] **$C_5H_5N_5O_2$**

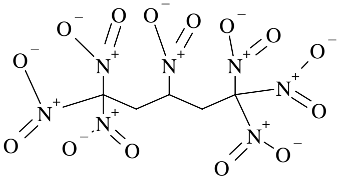


See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

1848. 1,1,1,3,5,5,5-Heptanitropentane

[20919-99-7] **$C_5H_5N_7O_{14}$**



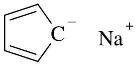
Klager, K. *et al., Propellants, Explos., Pyrotech.*, 1983, **8**, 25—28

This explosive compound has a +12% oxygen balance so can function as an oxidant.

See other OXIDANTS, POLYNITROALKYL COMPOUNDS

1849. Cyclopentadienylsodium

[4984-82-1] **C_5H_5Na**



King, R. B. *et al., Inorg. Synth.*, 1963, **7**, 101

The solid obtained by evaporation of the air-sensitive solution is pyrophoric in air.

See ALKALI-METAL DERIVATIVES OF HYDROCARBONS

Ammonium hexanitrocerate

See Sodium nitrate: Tetracyclopentadienylcerium

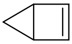
Lead(II) nitrate

See Lead(II) nitrate: Cyclopentadienylsodium

See other ALKYLMETALS, ORGANOMETALLICS

1850. Bicyclo[2.1.0]pent-2-ene

[5164-35-2] **C_5H_6**



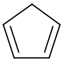
Andrist, A. H. *et al., Org. Synth.*, 1976, **55**, 18

A purified undiluted sample was reported to explode.

See other STRAINED-RING COMPOUNDS

†1851. Cyclopentadiene

[542-92-7] **C_5H_6**



HCS 1980, 348

1. Kirk-Othmer, 1965, Vol. 6, 690
2. Raistrick, B. *et al., J. Chem. Soc.*, 1939, 1761—1773
3. Starkie, A. *et al., Chem. in Brit.*, 1996, **32**(2), 35

Dimerisation is highly exothermic, the rate increasing rapidly with temperature, and may cause rupture of a closed uncooled container. The monomer may largely be prevented from dimerising by storage at —80°C or below [1]. The polymerisation of the undiluted diene may become explosive within the range 0—40°C and at pressures above 2300 bar. The effect of diluents was also studied [2]. A polymerisation was conducted with insufficient solvent, leading to a runaway and an explosion which killed three workers and destroyed plant up to 300 m away [3].

See Propene

See other POLYMERISATION INCIDENTS

Nitric acid

See Nitric acid: Hydrocarbons (reference 9)

Oxides of nitrogen

See Nitrogen oxide: Dienes, Oxygen

Dinitrogen tetraoxide: Hydrocarbons (reference 10)

Oxygen

Hock, H. *et al., Chem. Ber.*, 1951, **84**, 349

Exposure of the diene to oxygen gives peroxidic products containing some monomeric, but largely polymeric, peroxides, which explode strongly on contact with a flame.

See other POLYPEROXIDES

Oygen, Ozone

See Ozone: Dienes, Oxygen

Potassium hydroxide

Wilson, P. J. *et al., Chem. Rev.*, 1944, **34**, 8

Contact with the ethanolic base causes vigorously exothermic resin formation.

See other POLYMERISATION INCIDENTS

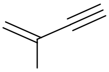
Sulfuric acid

See Sulfuric acid: Cyclopentadiene

See other DIENES

†1852. 2-Methyl-1-buten-3-yne

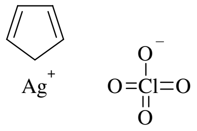
[78-80-8] **C_5H_6**



See other ALKYNES

1853. Cyclopentadiene—silver perchlorate

[ ] **$C_5H_6AgClO_4$**



Ulbricht, T. L. V., *Chem. & Ind.*, 1961, 1570

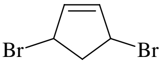
The complex explodes on heating.

See other SILVER COMPOUNDS

See related METAL PERCHLORATES

1854. 3,5-Dibromocyclopentene

[1890-04-6] **$C_5H_6Br_2$**



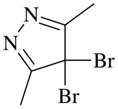
Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: 3,5-Dibromocyclopentene

See other HALOALKENES

1855. 4,4-Dibromo-3,5-dimethylpyrazole

[84691-20-3] **$C_5H_6Br_2N_2$**

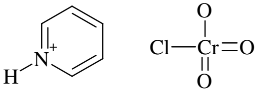


Adam, W. A. *et al., J. Org. Chem.*, 1994, **59**(23), 7067

This compound decomposed in a few days at —18°C. On warming to ambient it decomposed rapidly, exploding on one occasion.

1856. Pyridinium chlorochromate

[26299-14-9] **$C_5H_6ClCrNO_3$**

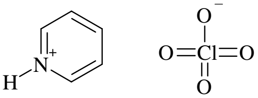


1. Glaros, G., *J. Chem. Educ.*, 1978, **55**, 410
2. Singh, J. H. *et al., Chem. & Ind.*, 1986, 751

It is a stable and safe oxidant which can replace oxodiperoxodipyridinechromium(VI) in oxidation of alcohols to aldehydes [1]. The quinolinium analogue has also found similar application [2].

See Oxodiperoxodipyridinechromium(VI)
See other OXIDANTS, QUATERNARY OXIDANTS

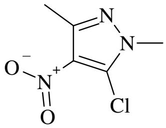
1857. Pyridinium perchlorate
[15598-34-2] **$C_5H_6ClNO_4$**



1. Kuhn, R. *et al., Chem. Ztg.*, 1950, **74**, 139
2. Anon., *Sichere Chemiearb.*, 1963, **15**(3), 19
3. Arndt, F. *et al., Chem. Ztg.*, 1950, **74**, 140
4. Schumacher, 1960, 213
5. Zacherl, M. K., *Mikrochemie*, 1948, **33**, 387—388
6. Anon., Private communication, 1991

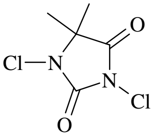
It can be detonated on impact, but is normally considered a stable intermediate (m.p. 288°C), suitable for purification of pyridine [1]. Occasionally explosions have occurred when the salt was disturbed [2], which have been variously attributed to presence of ethyl perchlorate, ammonium perchlorate, or chlorates. A sample was being dried in a glass vacuum desiccator. Over-enthusiastic release of vacuum distributed some of the salt onto the lid. The grinding action as the lid was slid off initiated explosion of this, shattering the lid [6]. A safer preparative modification is described [3]. It explodes on heating to above 335°C, or at a lower temperature if ammonium perchlorate is present [4]. A violent explosion which occurred during the final distillation according to the preferred method [3] was recorded [5].
See other PERCHLORATE SALTS OF NITROGENOUS BASES

1858. 5-Chloro-1,3-dimethyl-4-nitro-1 *H*-pyrazole
[13551-73-0] **$C_5H_6ClN_3O_2$**



See NITRATION INCIDENTS (reference 8)
See other C—NITRO COMPOUNDS

1859. 1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione
[118-52-5] **$C_5H_6Cl_2N_2O_2$**



Xylene

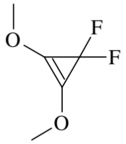
1. Anon., *Chem. Trade J.*, 1951, **129**, 136
2. *See entry* SELF-ACCELERATING REACTIONS

An attempt to chlorinate xylene with the 'dichlorohydantoin' caused a violent explosion [1]. The haloimide undergoes immediate self accelerating decomposition in presence of solvents. Safe conditions (including lower temperatures and progressive addition of reagent to match its consumption) can be developed for its use [2].

See other *N*-HALOIMIDES

1860. 3,3-Difluoro-1,2-dimethoxycyclopropene

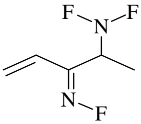
[59034-33-2] **$C_5H_6F_2O_2$**



See entry FLUORINATED CYCLOPROPENYL METHYL ETHERS

1861. 4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene

[33364-51-1] **$C_5H_6F_5N_3$**



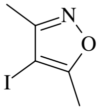
Parker, C. O. *et al., J. Org. Chem.*, 1972, **37**, 922

Samples of this and related poly-difluoroamino compounds exploded during analytical combustion.

See other DIFLUOROAMINO COMPOUNDS, *N*-HALOGEN COMPOUNDS

1862. 4-Iodo-3,5-dimethylisoxazole

[10557-85-4] **C_5H_6INO**



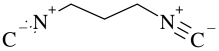
Peroxytrifluoroacetic acid

See Peroxytrifluoroacetic acid: 4-Iodo-3,5-dimethylisoxazole

See other IODINE COMPOUNDS, N—O COMPOUNDS

1863. 1,3-Diisocyanopropane

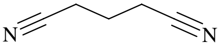
[72399-85-0] **$C_5H_6N_2$**



See entry DIISOCYANIDE LIGANDS

1864. Glutarodinitrile

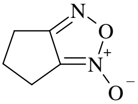
[544-13-8] **$C_5H_6N_2$**



Energy of decomposition (in range 200—340°C) measured as 0.098 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other CYANO COMPOUNDS

1865. 4,5-Cyclopentanofurazan-*N*-oxide (Trimethylenefuroxan)

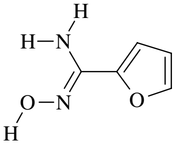
[54573-23-8] **$C_5H_6N_2O_2$**



Barnes, J. F. *et al., J. Chem. Res. (S)*, 1979, 314—315
It decomposes explosively on attempted distillation at 150°C at ambient pressure.
See other FURAZAN *N*-OXIDES

1866. Furan-2-amidoxime

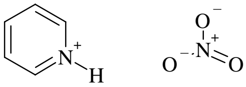
[50892-99-4] **$C_5H_6N_2O_2$**



Pearse, G. A., *Chem. Brit.*, 1984, **20**, 30
Attempted vacuum distillation of the oxime at a pot temperature of 100°C led to an explosion as distillation began. When heated at ambient pressure to above 65°C, a rapid exotherm occurs with gas evolution.
See other GAS EVOLUTION INCIDENTS, OXIMES

1867. Pyridinium nitrate

[543-53-3] **$C_5H_6N_2O_3$**



Goldstein, N. *et al., J. Chem. Phys.*, 1979, **70**, 5073

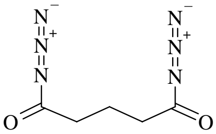
Like the perchlorate salt, pyridinium nitrate explodes on heating, but not with shock or friction.

See Pyridinium perchlorate

See other OXOSALTS OF NITROGENOUS BASES

1868. Glutaryl diazide

[64624-44-8] **$C_5H_6N_6O_2$**



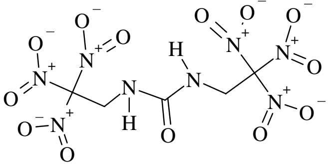
Curtiss, T. *et al., J. Prakt. Chem.*, 1900, **62**, 196

A very small sample exploded sharply on heating.

See other ACYL AZIDES

1869. *N,N′*-Bis(2,2,2-trinitroethyl)urea

[918-99-0] **$C_5H_6N_8O_{13}$**



Sodium hydroxide

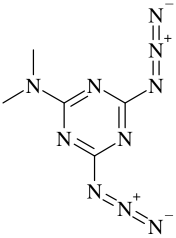
Biasutti, G. S., private comm., 1981

A pilot plant for manufacture of the title compound (an explosive of zero oxygen balance) was decommissioned and treated with concentrated alkali, but not completely drained. After 4 years, an explosion occurred, attributed to the hydrolytic formation of trinitroethanol or its sodium salt(s).

See 2,2,2-Trinitroethanol

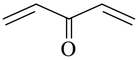
See other POLYNITROALKYL COMPOUNDS

1870. 2,4-Diazido-6-dimethylamino-1,3,5-triazine
[83297-43-2] **$C_5H_6N_{10}$**



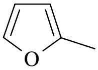
Preparative hazard
See 2,4,6-Triazido-1,3,5-triazine
See other ORGANIC AZIDES

1871. Divinyl ketone (1,4-Pentadien-3-one)
[1890-28-4] **C_5H_6O**

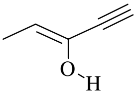


Trinitromethane
See Trinitromethane: Divinyl ketone

†1872. 2-Methylfuran
[534-22-5] **C_5H_6O**

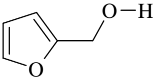


1873. 2-Penten-4-yn-3-ol
[101672-20-2] **C_5H_6O**



Brandsma, 1971, 73
The residue from distillation at 20 mbar exploded vigorously at above 90°C.
See other ACETYLENIC COMPOUNDS

1874. Furfuryl alcohol (2-Furanemethanol)
[98-00-0] **$C_5H_6O_2$**



Acids

1. Tobie, W. C., *Chem. Eng. News*, 1940, **18**, 72
2. *MCA Case History No. 858*
3. Dunlop, 1953, 214, 221, 783
4. Golosova, L. V., *Chem. Abs.*, 1975, **83**, 194098

A mixture of the alcohol with formic acid rapidly self-heated, then reacted violently [1]. A stirred mixture with cyanoacetic acid exploded violently after application of heat [2]. Contact with acids causes self-condensation of the alcohol, which may be explosively violent under unsuitable physical conditions. The general mechanism has been discussed [3]. The explosion hazards associated with the use of acidic catalysts to polymerise furfuryl alcohol may be avoided by using as catalyst the condensation product of 1,3-phenylenediamine and 1-chloro-2,3-epoxypropane [4].

See Nitric acid: Alcohols (reference 6)

See other POLYMERISATION INCIDENTS

Hydrogen peroxide

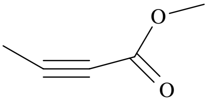
See Hydrogen peroxide: Alcohols

Sulfur tetrafluoride, Triethylamine

See Sulfur tetrafluoride: 2-(Hydroxymethyl)furan, Triethylamine

1875. Methyl 2-butynoate

[23326-27-4] **$C_5H_6O_2$**



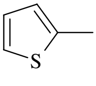
Cochran, J., *Chem. Eng. News* 1994, **72**(46), 4

Attempts to manufacture above the gram scale by several different routes have often resulted in violent decomposition during vacuum distillation. Distillation of more than a few grams demands caution.

See other ACETYLENIC COMPOUNDS

†1876. 2-Methylthiophene

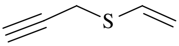
[554-14-3] **C_5H_6S**



Nitric acid

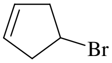
See Nitric acid: Methylthiophene

1877. 2-Propynyl vinyl sulfide
[21916-66-5] **C_5H_6S**



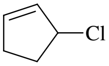
Brandsma, 1971, 7, 182
It decomposes explosively above 85°C.
See other ACETYLENIC COMPOUNDS

1878. 4-Bromocyclopentene
[1781-66-4] **C_5H_7Br**



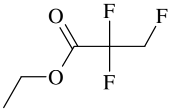
Preparative hazard
See Lithium tetrahydroaluminate: 3,5-Dibromocyclopentene
See other HALOALKENES

1879. 3-Chlorocyclopentene
[96-40-2] **C_5H_7Cl**



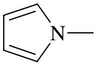
MCA Guide, 1972, 305
A 35 g portion decomposed (or polymerised) explosively after storage for 1 day.
See other HALOALKENES

1880. Ethyl 2,2,3-trifluoropropionate
[28781-86-4] **$C_5H_7F_3O_2$**



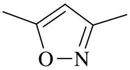
Sodium hydride
See Sodium hydride: Ethyl 2,2,3-trifluoropropionate

†1881. 1-Methylpyrrole
[96-54-8] **C_5H_7N**



1882. 3,5-Dimethylisoxazole

[300-87-8] **C_5H_7NO**



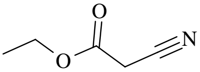
Sealed samples decompose exothermally above 210°C.

See entry ISOXAZOLES

See other N—O COMPOUNDS

1883. Ethyl cyanoacetate

[105-56-6] **$C_5H_7NO_2$**



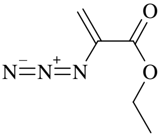
Preparative hazard

See Ethyl chloroacetate: Sodium cyanide

See other CYANO COMPOUNDS

1884. Ethyl 2-azido-2-propenoate

[81852-50-8] **$C_5H_7N_3O_2$**



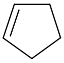
Kakimoto, M. *et al., Chem. Lett.*, 1982, 525—526

Attempted distillation caused a severe explosion; such materials should be purified without heating.

See other 2-AZIDOCARBONYL COMPOUNDS

†1885. Cyclopentene

[142-29-0] **C_5H_8**

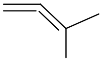


HCS 1980, 350

See other ALKENES

†1886. 3-Methyl-1,2-butadiene

[598-25-4] **C_5H_8**

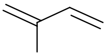


It is rather endothermic (ΔH_f° (g) +129.7 kJ/mol, 1.90 kJ/g).

See other DIENES, ENDOTHERMIC COMPOUNDS

†1887. 2-Methyl-1,3-butadiene (Isoprene)

[78-79-5] **C_5H_8**



FPA H112, 1982; *HCS 1980*, 573

Kirk-Othmer, 1967, Vol. 12, 79
It is somewhat endothermic, ΔH_f° (g) +75.7 kJ/mol, 1.11 kJ/g. In absence of inhibitors, isoprene absorbs atmospheric oxygen to form peroxides which do not separate from solution. Although the solution is not detonable, the gummy peroxidic polymer obtained by evaporation can be detonated by impact under standard conditions.
See 1,3-Butadiene (reference 2)

Acetone
Lokhmacheva, I. K. *et al., Chem. Abs.*, 1975, **82**, 63856
Prevention of peroxidation of isoprene—acetone mixtures, and other hazards involved in the industrial preparation of synthetic citral, are discussed.

Other reactants
Yoshida, 1980, 40
MRH values calculated for 14 combinations with oxidants are given.

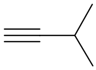
Oxygen, Ozone
See Ozone: Dienes, Oxygen

Ozone
Loveland, J. W., *Chem. Eng. News*, 1956, **34**(3), 292
Isoprene (1 g) dissolved in heptane was ozonised at —78°C. Soon after cooling was stopped, a violent explosion, followed by a lighter one, occurred. This was attributed to high concentrations of peroxides and ozonides building up at the rather low temperature employed. Operation at a higher temperature would permit the ozonides and peroxides to decompose, so avoiding high concentrations in the reaction mixture.
See other OZONIDES

Vinylamine
See Vinylamine: Isoprene
See other DIENES, ENDOTHERMIC COMPOUNDS

†1888. 3-Methyl-1-butyne

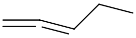
[598-23-2] **C_5H_8**



It is considerably endothermic, ΔH_f° (g) +136.4 kJ/mol, 2.0 kJ/g.
See other ALKYNES, ENDOTHERMIC COMPOUNDS

†1889. 1,2-Pentadiene

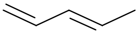
[591-95-7] **C_5H_8**



It is considerably endothermic, ΔH_f° (g) +145.6 kJ/mol, 2.14 kJ/g.
See other DIENES, ENDOTHERMIC COMPOUNDS

†1890. 1,3-Pentadiene

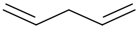
[504-60-9] **C_5H_8**



It is somewhat endothermic, ΔH_f° (g) +77.8 kJ/mol, 1.14 kJ/g.
See other DIENES, ENDOTHERMIC COMPOUNDS

†1891. 1,4-Pentadiene

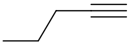
[591-93-5] **C_5H_8**



It is somewhat endothermic, ΔH_f° (g) +105.4 kJ/mol, 1.55 kJ/g.
See other DIENES, ENDOTHERMIC COMPOUNDS

†1892. 1-Pentyne

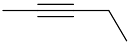
[627-19-0] **C_5H_8**



It is somewhat endothermic, ΔH_f° (g) +144.3 kJ/mol, 2.12 kJ/g.
See other ALKYNES, ENDOTHERMIC COMPOUNDS

†1893. 2-Pentyne

[627-21-4] **C_5H_8**



It is somewhat endothermic, ΔH_f° (g) +128.9 kJ/mol, 1.89 kJ/g.

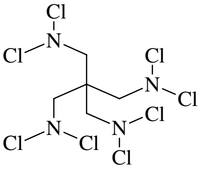
Mercury, Silver perchlorate

See Silver perchlorate: Alkynes, etc.

See other ALKYNES, ENDOTHERMIC COMPOUNDS

1894. Tetrakis(*N,N*-dichloroaminomethyl)methane

[ ] **$C_5H_8Cl_8N_4$**



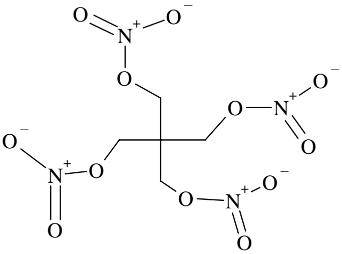
Lévy, R. S. *et al., Mém. Poudres*, 1958, **40**, 109

Shock- and heat-sensitive, it is a brisant more powerful than mercury fulminate.

See other *N*-HALOGEN COMPOUNDS

1895. 2,2-Bis[(nitrooxy)methyl]propane-1,3-diol dinitrate

[78-11-5] **$C_5H_8N_4O_{12}$**

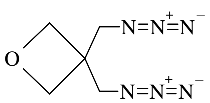


This heart drug (—14.3% oxygen balance) enjoys larger scale use as the explosive PETN (PentaErythritolTetraNitrate).

See other ALKYL NITRATES

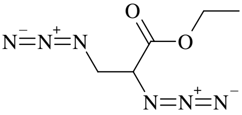
1896. 3,3-Bis(azidomethyl)oxetane

[17607-20-4] **$C_5H_8N_6O$**



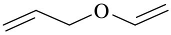
Frankel, M. B. *et al., J. Chem. Eng. Data*, 1981, **26**, 219
Explosive, of considerable sensitivity.
See other ORGANIC AZIDES

1897. Ethyl 2,3-diazidopropionate
[85590-62-1] **$C_5H_8N_6O_2$**



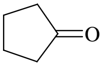
Owston. P. G. *et al., J. Chem. Res., Synop.*, 1985, 352—353
It is unstable and potentially explosive: routine use of a fume cupboard and safety screens is recommended.
See other 2-AZIDOCARBONYL COMPOUNDS, ORGANIC AZIDES

†1898. Allyl vinyl ether (3-Ethenoxypropene)
[3917-15-5] **C_5H_8O**



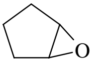
See other ALLYL COMPOUNDS

1899. Cyclopentanone
[120-92-3] **C_5H_8O**



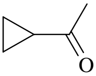
Hydrogen peroxide, Nitric acid
See Hydrogen peroxide: Ketones, etc.

†1900. Cyclopentene oxide (6-Oxabicyclo[3.1.0]hexane)
[285-67-6] **C_5H_8O**



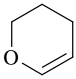
See other 1,2-EPOXIDES

†1901. Cyclopropyl methyl ketone
[765-43-5] **C_5H_8O**



†1902. 2,3-Dihydropyran

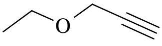
[110-87-2] **C_5H_8O**



HCS 1980, 410

1903. 1-Ethoxy-2-propyne

[628-33-1] **C_5H_8O**



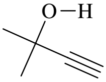
Brandsma, 1971, 172

Distillation of a 1 kg quantity at 80°C/1 bar led to a violent explosion. As the compound had not been stored under nitrogen during the 3 weeks since preparation, peroxide formation was suspected.

See other ACETYLENIC COMPOUNDS, PEROXIDISABLE COMPOUNDS

†1904. 2-Methyl-3-butyn-2-ol

[115-19-5] **C_5H_8O**



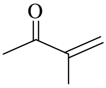
Sulfur tetrafluoride

See Sulfur tetrafluoride: 2-Methyl-3-butyn-2-ol

See other ACETYLENIC COMPOUNDS

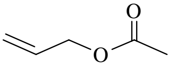
†1905. Methyl isopropenyl ketone (2-Methylbuten-3-one)

[814-78-8] **C_5H_8O**



†1906. Allyl acetate

[591-87-7] **$C_5H_8O_2$**

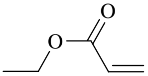


Energy of decomposition (in range 170—470°C) measured as 0.45 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other ALLYL COMPOUNDS

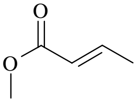
†1907. Ethyl acrylate (Ethyl propenoate)
[140-88-5] $C_5H_8O_2$



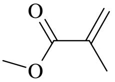
FPA H73, 1978; *HCS 1980*, 464

MCA Case History No. 1759
Inhibited monomer was transferred from a steel drum into a 4 l clear glass bottle exposed to sunlight in a laboratory in which the ambient temperature was temporarily higher than usual. Exothermic polymerisation set in and caused the bottle to burst. Precautions recommended included increase in inhibitor concentration tenfold (to 200 ppm) for laboratory-stored samples, and use of metal or brown glass containers.
See other POLYMERISATION INCIDENTS

†1908. Methyl crotonate (Methyl 2-butenoate)
[623-43-8] $C_5H_8O_2$



†1909. Methyl methacrylate (Methyl 2-methylpropenoate)
[80-62-6] $C_5H_8O_2$



FPA H62, 1977; *HCS 1980*, 656

1. Harmon, 1974, 2.13
2. Barnes, C. E. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 210
3. Bond, J., *Loss Prev. Bull.*, 1985, (065), 26
4. Huschke, D., *Chem. Processing* (Chicago), 1988, **51**(1), 136—137

The monomer tends to self polymerise and this may become explosive. It must be stored inhibited [1]. Exposure of the pure (unstabilised) monomer to air at ambient temperature for 2 months generated an ester—oxygen interpolymer, which exploded on evaporation of the surplus monomer at 60°C (but not at 40°C) [2]. Polymerisation, probably initiated by rust, in a drum of the monomer led to development of overpressure which sheared off the base and propelled the drum into the roof of the building [3]. Some oxygen must be present in the nitrogen used to inert storage tanks, to activate the stabiliser and prevent gelling of the monomer. Use of an

oxygen-selective permeable membrane to produce enriched nitrogen from compressed air for this purpose is described [4].
See Initiators, below
See also VIOLENT POLYMERISATION
See other POLYPEROXIDES

Dibenzoyl peroxide
See Dibenzoyl peroxide: Methyl methacrylate

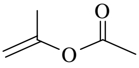
Initiators
1. Schulz, G. V. *et al., Z. Elektrochem.*, 1941, **47**, 749—761
2. Biesenberg, J. S. *et al., J. Polym. Eng. Sci.*, 1976, **16**, 101—116

Polymerisation of methyl methacrylate initiated by oxygen or peroxides proceeds with a steady increase in velocity during a variable induction period, at the end of which a violent 90°C exotherm occurs. This was attributed to an increase in chain branching, and not to a decrease in heat transfer arising from the increasing viscosity [1]. The parameters were determined in a batch reactor for thermal runaway polymerisation of methyl methacrylate, initiated by azoisobutyronitrile, dibenzoyl peroxide or di-*tert*-butyl peroxide [2].

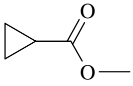
Other reactants
Yoshida, 1980, 359
MRH values calculated for 13 combinations with oxidants are given.

Propionaldehyde
CISHC Chem. Safety Summ., 1983, **54**(216), 498
Following an incident in which a drum containing bulked drainings (from other drums awaiting reconditioning) fumed and later exploded after sealing, it was found that methyl methacrylate and propionaldehyde can, under certain conditions of mixing, lead to a rapid exothermic reaction. Precautions are discussed.
See other POLYMERISATION INCIDENTS

†1910. Isopropenyl acetate
[108-72-5] **$C_5H_8O_2$**



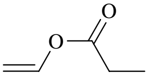
†1911. Methyl cyclopropanecarboxylate
[2868-37-3] **$C_5H_8O_2$**



See other STRAINED-RING COMPOUNDS

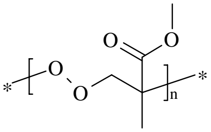
†1912. Vinyl propionate

[105-38-4] **$C_5H_8O_2$**



1913. Poly(methyl methacrylate peroxide)

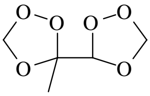
[ ] **$(C_5H_8O_4)_n$**



See also Methyl methacrylate (reference 2)
See POLYPEROXIDES

1914. Isoprene diozonide (3-(3-Methyl-1,2,4-trioxolan-3-yl)-1,2,4-trioxolane)

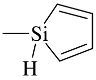
[118112-41-7] [118112-40-6] (diastereoisomers) **$C_5H_8O_6$**



See 2-Methyl-1,3-butadiene: Ozone
See other OZONIDES

1915. 1-Methylsilacyclopenta-2,4-diene (1-Methylsilole)

[72132-51-5] **C_5H_8Si**



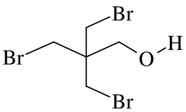
Dienophiles

Barton, T. J., *J. Organomet. Chem.*, 1979, **179**, C19

Thermal cracking at 150°C of the dimer (mixed isomers) of the silole in presence of reactive dienophiles (maleic anhydride, tetracyanoethylene or dimethyl acetylenedicarboxylate) inevitably produced violent explosions arising from exothermic Diels-Alder reactions.

1916. 2,2,2-Tris(bromomethyl)ethanol

[1522-92-5] **$C_5H_9Br_3O$**

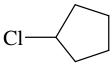


Ethyl acetoacetate, Zinc

See Ethyl acetoacetate: 2,2,2-Tris(bromomethyl)ethanol, Zinc

†1917. Chlorocyclopentane

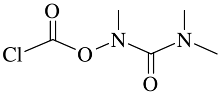
[930-28-9] **C_5H_9Cl**



See other HALOALKANES

1918. *N*-(Chlorocarbonyloxy)trimethylurea

[52716-12-8] **$C_5H_9ClN_2O_3$**



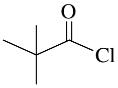
Groebner, P. *et al., Euro. J. Med. Chem., Chim. Ther.*, 1974, **9**, 32—34

A small sample decomposed explosively during vacuum distillation.

See other ACYL HALIDES, N—O COMPOUNDS

†1919. Pivaloyl chloride (Trimethylacetyl chloride)

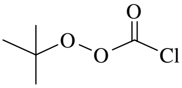
[3282-30-2] **C_5H_9ClO**



See other ACYL HALIDES

1920. *tert*-Butyl chloroperoxyformate

[56139-33-4] **$C_5H_9ClO_3$**



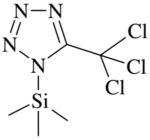
1. Bartlett, P. D. *et al., J. Amer. Chem. Soc.*, 1963, **85**, 1858
2. Hanson, P., *Chem. Brit.*, 1975, **11**, 418

The peroxyester is stable in storage at —25°C, and samples did not explode on friction, impact or heating. However, a 10 g sample stored at ambient temperature heated spontaneously, exploded and ignited [1]. A sample stored at —30°C exploded during manipulation at 0—5°C [2].

See other ACYL HALIDES, PEROXYESTERS

1921. 5-Trichloromethyl-1-trimethylsilyltetrazole

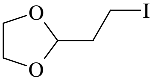
[72385-44-5] **$C_5H_9Cl_3N_4Si$**



Lazukina, L. A. *et al., J. Org. Chem. (USSR)*, 1980, **15**, 2009
It explodes at 80—90°C.
See other TETRAZOLES

1922. 2(2-Iodoethyl)-1,3-dioxolane

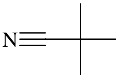
[83665-55-8] **$C_5H_9IO_2$**



Stowell, J. C. *et al., J. Org. Chem.*, 1983, **48**, 5382
Chromatographic purification on alumina is recommended because the compound decomposes with some violence on distillation at 55°C/1.6 mbar.
See other IODINE COMPOUNDS

†1923. Pivalonitrile (Trimethylacetonitrile)

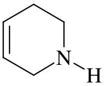
[630-18-2] **C_5H_9N**



See other CYANO COMPOUNDS

†1924. 1,2,3,6-Tetrahydropyridine

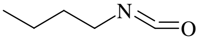
[694-05-3] **C_5H_9N**



See other ORGANIC BASES

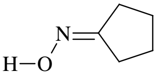
†1925. Butyl isocyanate

[111-36-4] **C_5H_9NO**



Energy of decomposition (in range 160—450°C) measured as 0.55 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ORGANIC ISOCYANATES

1926. Cyclopentanone oxime
[1192-28-5] **C_5H_9NO**



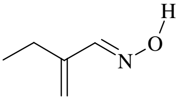
Sulfuric acid

1. Brookes, F. R., private comm., 1968
2. Peacock, C. J., private comm., 1978

Heating the oxime with 85% sulfuric acid to prepare 2-piperidone caused eruption of the stirred flask contents. Benzenesulfonyl chloride in alkali is a less vigorous reagent [1]. A similar reaction using 70% acid and methanol solvent proceeded uneventfully until vacuum distillation to remove volatiles had been completed at 90°C (bath)/ 27 mbar when the dark residue exploded [2].

See other OXIMES

1927. 2-Ethylacryladehyde oxime (2-Methylenebutanal oxime)
[99705-27-8] **C_5H_9NO**

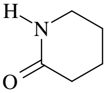


Marvel, C. S. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 5408

An explosion during distillation was recorded, possibly attributable to peroxide formation (or to Beckmann rearrangement).

See other OXIMES, PEROXIDISABLE COMPOUNDS

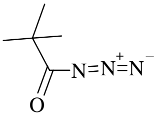
1928. 2-Piperidone
[675-20-7] **C_5H_9NO**



Preparative hazard

See Cyclopentanone oxime: Sulfuric acid

1929. Pivaloyl azide (Trimethylacetyl azide)
[4981-48-0] **$C_5H_9N_3O$**



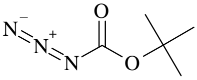
Bühler, A. *et al., Helv. Chim. Acta*, 1943, **26**, 2123

The azide exploded very violently on warming, and on one occasion, on standing.

See other ACYL AZIDES

1930. *tert*-Butyl azidoformate

[1070-19-5] **$C_5H_9N_3O_2$**



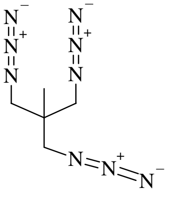
1. Carpino, L. A. *et al., Org. Synth.*, 1964, **44**, 15
2. Sakai, K. *et al., J. Org. Chem.*, 1971, **36**, 2387
3. Insalaco, M. A. *et al., Org. Synth.*, 1970, **50**, 12
4. Yajima, H. *et al., Chem. Pharm. Bull.*, 1970, **18**, 850—851
5. Fenlon, W. J., *Chem. Eng. News*, 1976, **54**(22), 3
6. Koppel, H. C., *Chem. Eng. News*, 1976, **54**(39), 5
7. Aldrich advertisement, *J. Chem. Soc., Chem. Comm.*, 1976, (23), i
8. Anon., *Org. Synth.*, 1977, **57**, 122
9. Aldrich advertisement, *J. Org. Chem.*, 1979, **44**(3), cover iv
10. Feyen, P., *Angew. Chem. (Intern. Ed.)*, 1977, **16**, 115

Explosion during distillation at 74°C/92 mbar had been recorded on only one out of several hundred occasions [1], but an alternative procedure avoiding distillation has been described [2]. Although distillation at 56—71°C/53 mbar has been accomplished on many occasions, the structure of the compound suggests that it should be considered as potentially explosive [3]. It is important in the preparation to eliminate all traces of phosgene before adding sodium azide to avoid formation of the dangerously explosive carbonyl azide [4]. The undiluted compound is a shock-sensitive explosive, which is thermally unstable between 100 and 135°C and autoignites at 143°C [5]. A safer reagent for *tert*-butoxycarbonylation of amino groups was then made available [6,7], and other safer alternatives are also available [8], including di-*tert*-butyl dicarbonate [9]. An explosion during evaporation of an ethereal solution of the azide at 50°C has also been reported [10].

See other ACYL AZIDES

1931. 1,1,1-Tris(azidomethyl)ethane

[31044-86-7] **$C_5H_9N_9$**



Hydrogen, Palladium catalyst.

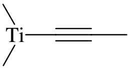
Zompa, L. J. *et al., Org. Prep. Proced. Int.*, 1974, **6**, 103—106

There is an explosion hazard during the palladium-catalysed hydrogenation of the tris-azide in ethanol at 2 bar to the tris-amine.

See other CATALYTIC NITRO REDUCTION PROCESSES, HYDROGENATION INCIDENTS, ORGANIC AZIDES

1932. Dimethyl-1-propynylthallium

[ ] **C_5H_9Tl**



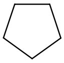
Nast, R. *et al., J. Organomet. Chem.*, 1966, **6**, 461

It explodes on heating and is sensitive to stirring or impact.

See other ALKYLMETALS, METAL ACETYLIDES

†1933. Cyclopentane

[287-92-3] **C_5H_{10}**



HCS 1980, 349

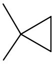
Other reactants

Yoshida, 1980, 154

MRH values calculated for 13 combinations with oxidants are given.

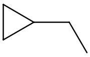
†1934. 1,1-Dimethylcyclopropane

[1630-94-0] **C_5H_{10}**



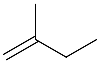
†1935. Ethylcyclopropane

[1191-96-4] **C_5H_{10}**



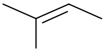
†1936. 2-Methyl-1-butene

[563-46-2] **C_5H_{10}**

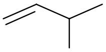


†1937. 2-Methyl-2-butene

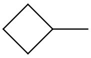
[513-35-9] **C_5H_{10}**



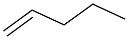
†1938. 3-Methyl-1-butene
[563-45-1] **C_5H_{10}**



†1939. Methylcyclobutane
[598-61-8] **C_5H_{10}**

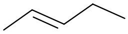


†1940. 1-Pentene
[109-67-1] **C_5H_{10}**

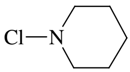


HCS 1980, 718

†1941. 2-Pentene
[646-04-8] **C_5H_{10}**



1942. *N*-Chloropiperidine
[2156-71-0] **$C_5H_{10}ClN$**

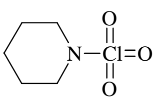


Claxton, G. P. *et al., Org. Synth.*, 1977, **56**, 120

To avoid rapid spontaneous decomposition of the compound, solvent ether must only be partially distilled out of the extracted product, and from a water bath maintained at below 60°C.

See other *N*-HALOGEN COMPOUNDS

1943. *N*-Perchlorylpiperidine
[768-34-3] **$C_5H_{10}ClNO_3$**



Alone, or Piperidine

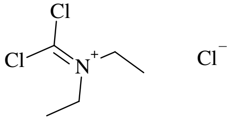
Gardner, D. L. *et al., J. Org. Chem.*, 1964, **29**, 3738—3739

It is a dangerously sensitive oil which has exploded on storage, heating or contact with piperidine. Absorption in alumina was necessary to desensitise it to allow non-explosive analytical combustion.

See other PERCHLORYL COMPOUNDS

1944. Dichloromethylenediethylammonium chloride

[33842-02-3] **$C_5H_{10}Cl_3N$**

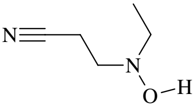


1. Bader, A. R., private comm., 1971
2. Viehe, H. G. *et al., Angew. Chem. (Intern. Ed.)*, 1971, **10**, 573

The compound does not explode on heating [1], the published statement [2] is in error.

1945. *N*-(2-Cyanoethyl)ethylhydroxylamine

[ ] **$C_5H_{10}N_2O$**



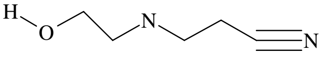
Krueger H., *Chem. Abs.*, 1998, **128**, 92406z

Although this compound would undoubtedly be unstable, it here appears to be a misprint for the isomeric ethanolamine entered directly below.

See 3-(2-Hydroxyethylamino)propionitrile

1946. 3-(2-Hydroxyethylamino)propionitrile (*N*-(2-Cyanoethyl)ethanolamine)

[33759-44-3] **$C_5H_{10}N_2O$**

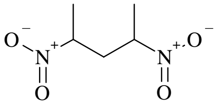


Krueger H., *Prax. Sicherheitstech.*, 1997, **4**, 83

A storage tank containing this compound self-heated, with evolution of ammonia, then burst with generation of polymer. The reaction appears to be autocatalytic generation of 2-vinyloxazoline, which then polymerises. Thermal analysis showed it unsafe for storage at 50°C, although storable at room temperature. Other homologues became increasingly stable as the distance between hydroxyl and amino groups increases.

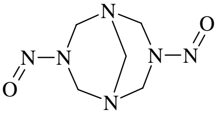
See other CYANO COMPOUNDS

1947. 2,4-Dinitropentane isomers
[109745-04-2] [109745-05-3] (R*,S* and R*,R* (±), resp.) **$C_5H_{10}N_2O_4$**



Wade, P. A. *et al., J. Amer. Chem. Soc.*, 1987, **109**, 5052—5055
A grossly impure sample of the (±) mixed isomers decomposed vigorously when distilled at 130°C. During steam distillation of the R*,S* isomer, overheating of the still pot caused vigorous decomposition: destruction of the pot residues with nitric acid was also vigorous for both.
See other POLYNITROALKYL COMPOUNDS

1948. 3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane
[101-25-7] **$C_5H_{10}N_6O_2$**

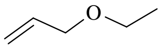


1. *MCA Case History No. 841*
2. *See entry* HIGH RATE DECOMPOSITION
3. Hancyk, B. *et al., Chem. Abs.*, 1988, **109**, 212215

A cardboard drum of the blowing agent 'dinitrosopentamethylenetetramine' (as a 40% dispersion in fine silica) ignited when roughly handled in storage [1]. It exhibits fast flame propagation on moderate heating, either neat or mixed with 20% chalk [2]. Mixtures with mineral dust (1:4) eliminated neither fire nor explosion hazards, and mixtures with liquid wax (1:4) eliminated explosion hazard but increased the flammability hazard. The neat blowing agent is highly sensitive to explosion if impacted or dropped. Thermal analysis showed that presence of desensitising agents had no effect on thermal stability and course of decomposition of the title compound, which at above 180°C undergoes self-accelerating decomposition [3]. The more recently calculated value of 78°C for the critical ignition temperature is in close agreement with the previous value of 75°C.
See entry CRITICAL IGNITION TEMPERATURE

Other reactants
Yoshida, 1980, 158
MRH values calculated for 11 mixtures with other materials (usually present in catalytic proportions) are given.
See other BLOWING AGENTS, NITROSO COMPOUNDS

†1949. Allyl ethyl ether (3-Ethoxypropene)
[557-31-3] **$C_5H_{10}O$**

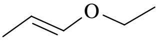


HCS 1980, 127

Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 7
A commercial sample was distilled without being tested for peroxides and exploded towards the end of distillation. It was later shown to contain peroxides.
See other PEROXIDISABLE COMPOUNDS

†1950. Ethyl propenyl ether (1-Ethoxypropene)

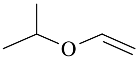
[928-55-2] **$C_5H_{10}O$**



See other PEROXIDISABLE COMPOUNDS

†1951. Isopropyl vinyl ether

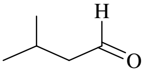
[926-65-8] **$C_5H_{10}O$**



See other PEROXIDISABLE COMPOUNDS

†1952. Isovaleraldehyde

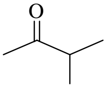
[590-86-3] **$C_5H_{10}O$**



See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

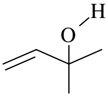
†1953. 3-Methyl-2-butanone

[563-80-4] **$C_5H_{10}O$**



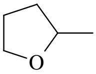
†1954. 2-Methyl-3-buten-2-ol

[115-18-4] **$C_5H_{10}O$**



†1955. 2-Methyltetrahydrofuran

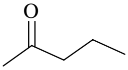
[96-47-9] **$C_5H_{10}O$**



See other PEROXIDISABLE COMPOUNDS

†1956. 2-Pentanone

[107-87-9] **$C_5H_{10}O$**



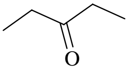
FPA H110, 1982; *HCS 1980*, 661

Bromine trifluoride
See Bromine trifluoride: 2-Pentanone

Other reactants
Yoshida 1980, 369
MRH values calculated for 13 combinations with oxidants are given.

†1957. 3-Pentanone

[96-22-0] **$C_5H_{10}O$**



HCS 1980, 401

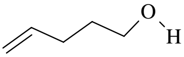
Hydrogen peroxide,	MRH 6.44/84
Nitric acid	MRH 5.82/79

See Hydrogen peroxide: Ketones, etc.

Other reactants
Yoshida, 1980, 338
MRH values calculated for 13 combinations with oxidants are given.

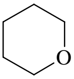
†1958. 4-Penten-1-ol

[821-09-0] **$C_5H_{10}O$**



†1959. Tetrahydropyran

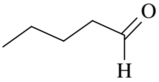
[142-68-7] **$C_5H_{10}O$**



See other PEROXIDISABLE COMPOUNDS

†1960. Valeraldehyde (Pentanal)

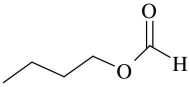
[110-62-3] **$C_5H_{10}O$**



See ALDEHYDES

†1961. Butyl formate

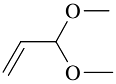
[592-84-7] **$C_5H_{10}O_2$**



HCS 1980, 247

†1962. 3,3-Dimethoxypropene

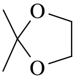
[6044-68-4] **$C_5H_{10}O_2$**



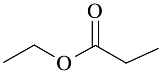
See other ALLYL COMPOUNDS, PEROXIDISABLE COMPOUNDS

†1963. 2,2-Dimethyl-1,3-dioxolane

[2916-31-6] **$C_5H_{10}O_2$**

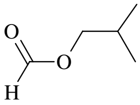


†1964. Ethyl propionate (Ethyl propanoate)
[105-37-3] **$C_5H_{10}O_2$**

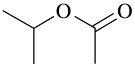


HCS 1980, 499

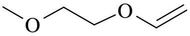
†1965. Isobutyl formate
[542-55-2] **$C_5H_{10}O_2$**



†1966. Isopropyl acetate
[108-21-4] **$C_5H_{10}O_2$**

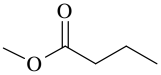


†1967. 2-Methoxyethyl vinyl ether
[1663-35-0] **$C_5H_{10}O_2$**

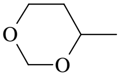


See other PEROXIDISABLE COMPOUNDS

†1968. Methyl butyrate
[623-42-7] **$C_5H_{10}O_2$**

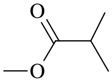


†1969. 4-Methyl-1,3-dioxane
[1120-97-4] **$C_5H_{10}O_2$**



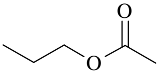
†1970. Methyl isobutyrate

[547-63-7] **$C_5H_{10}O_2$**



†1971. Propyl acetate

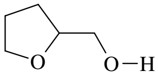
[109-60-4] **$C_5H_{10}O_2$**



HCS 1980, 795

1972. Tetrahydrofurfuryl alcohol

[97-99-4] **$C_5H_{10}O_2$**



HCS 1980, 892

3-Nitro-*N*-bromophthalimide

See *N*-HALOIMIDES: Alcohols

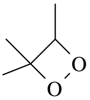
Other reactants

Yoshida, 1980, 239

MRH values calculated for 13 combinations with oxidants are given.

1973. Trimethyl-1,2-dioxetane

[22668-10-6] **$C_5H_{10}O_2$**

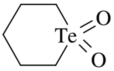


See 3,3-Dimethyl-1,2-dioxetane

See other CYCLIC PEROXIDES, DIOXETANES, STRAINED-RING COMPOUNDS

1974. Tellurane-1,1-dioxide

[ ] **$C_5H_{10}O_2Te$**



Alone, or Acids

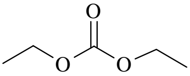
Morgan, G. T. *et al., J. Chem. Soc.*, 1928, 321

It exploded on rapid heating, and decomposed violently in contact with nitric or sulfuric acids.

See related ALKYLMETALS

†1975. Diethyl carbonate

[105-58-8] **$C_5H_{10}O_3$**



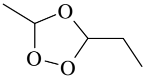
HCS 1980, 396

Norton, C., *Chemical Engineer*, 1995, (595), 6

A drum containing distillation wastes of ethyl carbonate, ethyl bromoacetate and another bromoester (not intelligibly named) burst spontaneously, releasing a cloud which caused considerable lachrymation and respiratory irritation in nearby housing. Carbon dioxide was doubtless generated, but whether by water contamination or a previously unknown catalytic reaction of the known contents is unclear to the editor.

1976a. *trans*-2-Pentene ozonide (3-Ethyl-5-methyl-1,2,4-trioxolane)

[16187-03-4] **$C_5H_{10}O_3$**

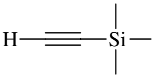


See trans-2-Hexene ozonide

See other OZONIDES

1976b. 1-Trimethylsilylethyne (Trimethylsilylacetylene)

[1066-54-2] **$C_5H_{10}Si$**



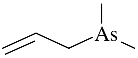
Blumenthal, S., *The Tech, (MIT)*, 1995, **115**(29), 1

An incident attributed to overheating a flask while distilling this is reported. It is implied that it was not really an explosion, but thermal stress shattering glass – however part of that glass was evidently projected a moderate distance with enough force to wound. Explosion indeed seems the right word (Ed.).

See other ACETYLENIC COMPOUNDS

1977. Allyldimethylarsine

[691-35-0] **$C_5H_{11}As$**



Ellern, 1968, 24—25

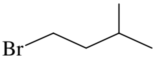
It ignites in air if exposed on filter paper.

See other ALLYL COMPOUNDS

See related ALKYLNON-METALS

†1978. 1-Bromo-3-methylbutane

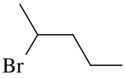
[107-82-4] **$C_5H_{11}Br$**



See other HALOALKANES

†1979. 2-Bromopentane

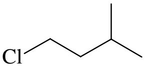
[107-81-3] **$C_5H_{11}Br$**



See other HALOALKANES

†1980. 1-Chloro-3-methylbutane

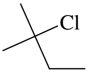
[107-84-6] **$C_5H_{11}Cl$**



See other HALOALKANES

†1981. 2-Chloro-2-methylbutane

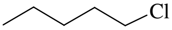
[594-36-5] **$C_5H_{11}Cl$**



See other HALOALKANES

†1982. 1-Chloropentane

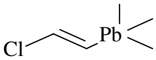
[543-59-9] **$C_5H_{11}Cl$**



See other HALOALKANES

1983. 2-Chlorovinyltrimethyllead

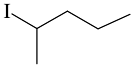
[ ] **$C_5H_{11}ClPb$**



Steingross, W. *et al., J. Organomet. Chem.*, 1966, **6**, 109
It may explode violently during vacuum distillation at 102°C/62.5 mbar.
See related ALKYLMETALS

†1984. 2-Iodopentane

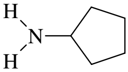
[637-97-8] **$C_5H_{11}I$**



See other HALOALKANES

†1985. Cyclopentylamine

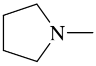
[1003-03-8] **$C_5H_{11}N$**



See other ORGANIC BASES

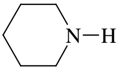
†1986. *N*-Methylpyrrolidine

[120-94-5] **$C_5H_{11}N$**



See other ORGANIC BASES

†1987. Piperidine
[110-89-4] **$C_5H_{11}N$**



HCS 1980, 757

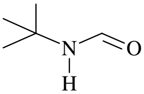
Dicyanofurazan
See Dicyanofurazan: Nitrogenous bases

N-Nitrosoacetanilide
See N-Nitrosoacetanilide: Piperidine

Other reactants
Yoshida, 1980, 291
MRH values calculated for 13 combinations with oxidants are given.

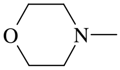
N-Perchlorylpiperidine
See N-Perchlorylpiperidine: Alone, etc.
See other ORGANIC BASES

1988. *N-tert*-Butylformamide
[2425-74-3] **$C_5H_{11}NO$**



Di-*tert*-butyl hyponitrite
See trans-Di-*tert*-butyl hyponitrite: Formamides

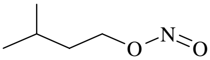
†1989. 4-Methylmorpholine
[109-02-4] **$C_5H_{11}NO$**



HCS 1980, 657

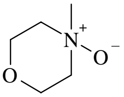
See other ORGANIC BASES

†1990. Isopentyl nitrite
[110-46-3] **$C_5H_{11}NO_2$**



See other ALKYL NITRITES

1991. *N*-Methylmorpholine oxide (4-Methylmorpholine-4-oxide)
[7529-22-8] [70187-32-5], [85489-61-8], [80913-66-2], [80913-65-1] (hydrates); [95650-61-6] (cellulose complex) **C5H11NO2**



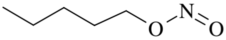
Cellulose

1. Peguy, A. *et al., J. Appl. Poly, Science*, 1990, **40**(3/4), 429
2. Kalt, W. *et al., Austrian Patent*, AT 9301857; WO Appl. 95/08010

Solutions of cellulose in wet methylmorpholine oxide can undergo exothermic reaction to the point of explosion if confined at elevated temperatures from about 120°C, or if otherwise heated to 180°C. The reaction is catalysed by some metals, notably copper [1]. Many stabilisers for the system have been claimed, the preamble to the patent [2] contains an extensive review of these and of germane academic literature on the decomposition reactions.

See other CATALYTIC IMPURITY INCIDENTS, *N*-OXIDES

†1992. Pentyl nitrite
[463-04-7] **$C_5H_{11}NO_2$**

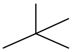


Sorbe, 1968, 146

It explodes on heating to above 250°C.

See other ALKYL NITRITES

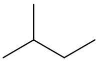
†1993. 2,2-Dimethylpropane (Neopentane)
[463-82-1] **C_5H_{12}**



Preparative hazard

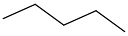
See Aluminium: Halocarbons (reference 9)

†1994. 2-Methylbutane (Isopentane)
[78-78-4] **C_5H_{12}**



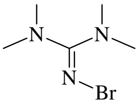
HCS 1980, 572

†1995. Pentane
[109-66-0] **C_5H_{12}**



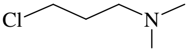
FPA H55, 1977; *HCS 1980*, 716

1996. *N*-Bromotetramethylguanidine
[6926-40-5] **$C_5H_{12}BrN_3$**



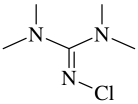
Papa, A. J., *J. Org. Chem.*, 1966, **31**, 1426
The material is unstable even at 0°C, and explodes if heated above 50°C at ambient pressure.
See other *N*-HALOGEN COMPOUNDS

1997. 1-Chloro-3-dimethylaminopropane
[109-54-6] **$C_5H_{12}ClN$**



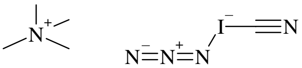
Lithium, Sodium
See Lithium: 1-Chloro-3-dimethylaminopropane, etc.

1998. *N*-Chlorotetramethylguanidine
[6926-39-2] **$C_5H_{12}ClN_3$**



Papa, A. J., *J. Org. Chem.*, 1961, **31**, 1426
The material is unstable even at 0°C, and explodes if heated above 50°C at ambient pressure.
See other *N*-HALOGEN COMPOUNDS

1999. Tetramethylammonium azidocyanoiodate(I)
[68574-17-4] **$C_5H_{12}IN_5$**



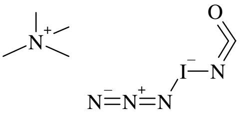
Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 512

This, and the cyanato and selenocyanato (pseudohalogen) analogues are explosive in the solid state, but may be handled with comparative safety. They are also sensitive to laser light.

See related METAL AZIDES

2000. Tetramethylammonium azidocyanatoiodate(I)

[68574-15-2] **$C_5H_{12}IN_5O$**

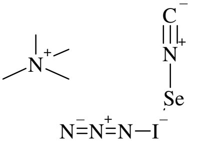


See Tetramethylammonium azidocyanoiodate(I), above

See related METAL AZIDES, METAL CYANATES

2001a. Tetramethylammonium azidoselenocyanatoiodate(I)

[ ] **$C_5H_{12}IN_5Se$**

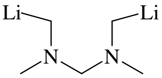


See Tetramethylammonium azidocyanoiodate(I)

See related METAL AZIDES, METAL CYANATES

2001b. Di(*N*-lithiomethyl-*N*-methylamino)methane

[ ] **$C_5H_{12}Li_2N_2$**

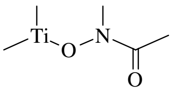


Denk, M. K. *et al.*, Chem. Eng. News, 2003, 81(26) 2

This compound exploded during vacuum drying. It is considered that solvation may be a stabilising factor and drying should be avoided.

2002. Dimethylthallium *N*-methylacetohydroxamate

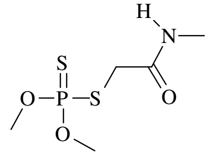
[57812-15-4] **$C_5H_{12}NO_2Tl$**



Schwering, H. U. *et al., J. Organomet. Chem.*, 1975, **99**, 22

It exploded below 160°C, without melting, unlike the other dialkyl- gallium and indium derivatives, which showed notable thermal stability.
See other N—O COMPOUNDS

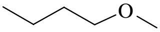
2003. *O,O*-Dimethyl *S*-methylcarbamoylmethyl phosphorodithioate
[60-51-5] **$C_5H_{12}NO_3PS_2$**



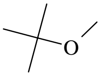
1. Matos, E. *et al., Chem. Abs.*, 1983, **98**, 94955
2. Ludovisi, G, *et al.* in *Safety and Runaway Reactions*, Smeder, B & Mitchison, N. (Eds.), EUR 17723 EN, European Commission, 1997, p11

Accidental exothermic decomposition of the insecticide Dimethoate in a 6000 l vessel led to gross contamination; (no further details of circumstances available from author) [1]. A second incident of bulk decomposition in cyclohexanone solution (concentration not given) is slightly better reported. This was a formulation solution; the details of the processing are not clear from the report but appear to have involved azeotroping the dimethoate dry, then discharging the warm solution (no temperatures given) to the insulated, uncooled, storage vessel which burst. It is claimed that out of specification material had been processed at above previous temperatures. In any event, there was a runaway exotherm, loss of containment, fire, the attentions of regulatory authorities and closure of the factory. The manufacturer's safety study went beyond the then legal requirements, but, as so often, concentrated on toxicity while neglecting the reactivity which could cast that toxicity abroad. A laboratory sample of the liquid residue of the accident itself later burst its container [2].
See also THIONOESTERS
See other PHOSPHORUS ESTERS

†2004. Butyl methyl ether
[628-28-4] **$C_5H_{12}O$**



†2005. *tert*-Butyl methyl ether
[1634-04-4] **$C_5H_{12}O$**



1. Hage, T., *Chem. Abs.*, 1987, **107**, 21833
2. Pearson, H., *Chem. Abs.*, 1988, **108**, 115254

tert-Butyl methyl ether, now manufactured in bulk as a gasoline component, is a less hazardous extracting solvent than diethyl ether, as it scarcely forms peroxides, is less volatile (b.p. 55°C) and has a narrower flammable range (2.5—15%) in air [1]. However, fires involving it are difficult to extinguish with foam, as no film-forming effect is shown [2].

Acid chlorides

It seems probable that the reaction with sulfinyl chloride (below) is an example of a more general phenomenon.

Sulfinyl chloride

See Sulfinyl chloride: *tert*-Butyl methyl ether

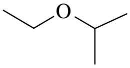
Sulfuric acid

Anon., *Eur. Chem. News*, 1995, **64**(1678), 5

An explosion and fire, costing the life of one worker, occurred when sulphuric acid entered a distillation during scale-up (in glass) of a carotenoid synthesis. This caused a sudden rise in temperature and pressure, bursting the distillation column and an adjacent vessel containing methyl t-butyl ether. Reading between the lines: this was the solvent being distilled off; acid catalysis will cause it to revert to methanol and butene. Large scale glass apparatus may burst with overpressures as low as 0.2 bar.

†2006. Ethyl isopropyl ether

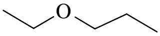
[625-54-7] **$C_5H_{12}O$**



See other PEROXIDISABLE COMPOUNDS

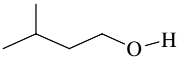
†2007. Ethyl propyl ether

[628-32-0] **$C_5H_{12}O$**



2008. Isopentanol (3-Methylbutanol)

[123-51-3] **$C_5H_{12}O$**

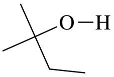


FPA H123, 1983; *HCS 1980*, 642

Hydrogen trisulfide

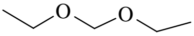
See Hydrogen trisulfide: Pentanol

†2009. *tert*-Pentanol (1,1-Dimethylpropanol)
[75-85-4] **$C_5H_{12}O$**

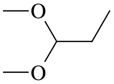


HCS 1980, 395

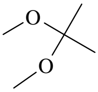
†2010. Diethoxymethane
[462-95-3] **$C_5H_{12}O_2$**



†2011. 1,1-Dimethoxypropane
[4744-10-9] **$C_5H_{12}O_2$**



†2012. 2,2-Dimethoxypropane
[77-76-9] **$C_5H_{12}O_2$**



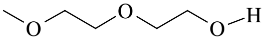
Becerra, R. *et al., An. Quim., Ser. A*, 1983, **79**, 163—167
The relationship between the cool flames observed at 210°C and subsequent explosions were studied.
See entry COOL FLAMES

Metal perchlorates

1. Dickinson, R. C. *et al., Chem. Eng. News*, 1970, **48**(28), 6
2. Cramer, R., *Chem. Eng. News*, 1970, **48**(45), 7
3. Mikulski, S. M., *Chem. Eng. News*, 1971, **49**(4), 8

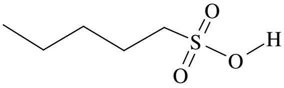
During dehydration of manganese(II) perchlorate [1] or nickel(II) perchlorate [2] with dimethoxypropane, heating above 65°C caused violent explosions, probably involving oxidation by the anion [1] (possibly of the methanol liberated by hydrolysis). Triethyl orthoformate is recommended as a safer dehydrating agent [2] (but methanol would still be liberated).
See Dimethyl sulfoxide: Metal oxosalts
See also METAL PERCHLORATES (reference 2)

2013. 2-(2-Methoxyethoxy)ethanol
[111-77-3] **$C_5H_{12}O_3$**



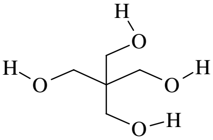
Calcium hypochlorite
See Calcium hypochlorite: Hydroxy compounds

2014. Pentanesulfonic acid
[35452-30-3] **$C_5H_{12}O_3S$**



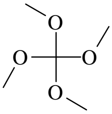
Preparative hazard
See Nitric acid: Alkanethiols (reference 3)
See other ORGANIC ACIDS

2015. Pentaerythritol
[115-77-5] **$C_5H_{12}O_4$**

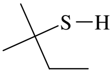


Thiophosphoryl chloride
See Thiophosphoryl chloride: Pentaerythritol

†2016. Tetramethyl orthocarbonate (Tetramethoxymethane)
[1850-14-2] **$C_5H_{12}O_4$**



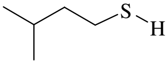
†2017. 2-Methylbutane-2-thiol
[1679-09-0] **$C_5H_{12}S$**



See other ALKANETHIOLS

†2018. 3-Methylbutanethiol

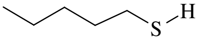
[541-31-1] **$C_5H_{12}S$**



See other ALKANETHIOLS

†2019. Pentanethiol

[110-66-7] **$C_5H_{12}S$**



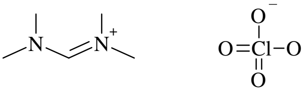
Nitric acid

See Nitric acid: Alkanethiols (reference 3)

See other ALKANETHIOLS

2020. *N,N,N′,N′*-Tetramethylformamidinium perchlorate

[2506-80-1] **$C_5H_{13}ClN_2O_4$**



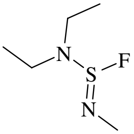
Menzer, M. *et al., Z. Chem.*, 1977, **17**, 344

The undeuterated salt was refluxed with deuterium oxide to effect deuterium exchange, then the excess was evaporated off under vacuum. Towards the end of the evaporation the moist residue exploded violently. The presence of D is not likely to affect instability of the structure.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

2021. *S*-Diethylamino(methylimino)sulfur(IV) fluoride

[ ] **$C_5H_{13}FNS$**

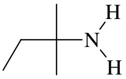


von Halasz, A. *et al., Chem. Ber.*, 1971, **104**, 1250, 1253

Care is necessary in the preparation, because if coloured impurities are present, the compound may polymerise violently and very exothermically at ambient temperature.

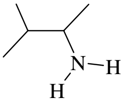
See other N—S COMPOUNDS

†2022. 1,1-Dimethylpropylamine
[594-39-8] **$C_5H_{13}N$**



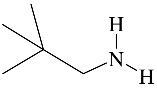
See other ORGANIC BASES

†2023. 1,2-Dimethylpropylamine
[598-74-3] **$C_5H_{13}N$**



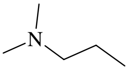
See other ORGANIC BASES

†2024. 2,2-Dimethylpropylamine (Neopentylamine)
[5813-64-9] **$C_5H_{13}N$**



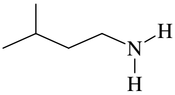
See other ORGANIC BASES

†2025. *N,N*-Dimethylpropylamine
[926-63-6] **$C_5H_{13}N$**



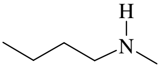
See other ORGANIC BASES

†2026. Isopentylamine
[107-85-7] **$C_5H_{13}N$**



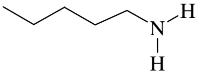
See other ORGANIC BASES

†2027. *N*-Methylbutylamine
[110-68-9] **$C_5H_{13}N$**



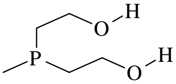
See other ORGANIC BASES

†2028. Pentylamine
[110-58-7] **$C_5H_{13}N$**



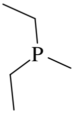
See other ORGANIC BASES

2029. Bis(2-hydroxyethyl)methylphosphine
[53490-67-8] **$C_5H_{13}O_2P$**



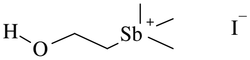
Dichloromethylphosphine
See Dichloromethylphosphine: Bis(2-hydroxyethyl)methylphosphine
See related ALKYLPHOSPHINES

2030. Diethylmethylphosphine
[1605-58-9] **$C_5H_{13}P$**



Personal experience
May ignite in air with long exposure.
See other ALKYLPHOSPHINES

2031. 2-Hydroxyethyltrimethylstibonium iodide
[81924-93-8] **$C_5H_{14}IOSb$**

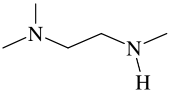


Meyer, E. M. *et al., Biochem. Pharm.*, 1981, **30**, 3003—3005

An attempt to prepare this antimony analogue of choline by heating trimethylstibine with iodoethanol in bis(2-methoxyethyl) ether in a sealed tube at 150°C led to an explosion.

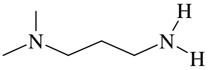
†2032. 2-Dimethylamino-*N*-methylethylamine

[142-25-6] **$C_5H_{14}N_2$**



2033. 3-Dimethylaminopropylamine

[109-55-7] **$C_5H_{14}N_2$**



HCS 1980, 423

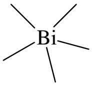
Cellulose nitrate
See CELLULOSE NITRATE: Amines

1,2-Dichloroethane
See 1,2-Dichloroethane: 3-Dimethylaminopropylamine

Other reactants
Yoshida, 1980, 168
MRH values calculated for 14 combinations with oxidants are given.

2034a. Pentamethylbismuth

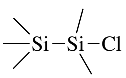
[148739-67-7] **$C_5H_{15}Bi$**



Seppelt, K. *et al., Angew. Chem. (Int.)*, 1994, **33**(9), 976
This compound, formed at —90°C is unstable in solution and the solid explodes on rapid warming to room temperature.
See other ALKYL METALS

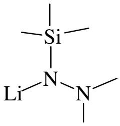
2034b. Chloropentamethyldisilane

1560-28-7 **C5H15ClSi2**



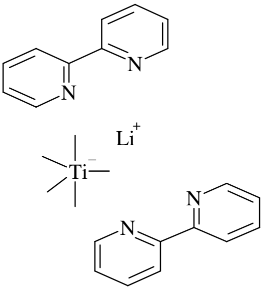
Horn, K. A. *Chem. Eng. News*, 1990, **68**(26), 2
Violent exotherms were observed when distilling this compound under nitrogen
See 1,2-Dichlorotetramethyldisilane
See other ALKYLHALOSILANES

2035. Lithium 2,2-dimethyltrimethylsilylhydrazide
[13529-75-4] **$C_5H_{15}LiN_2Si$**



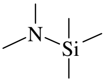
Oxidants
See entry SILYLHYDRAZINES

2036. Lithium pentamethyltitanate—bis(2,2'-bipyridine)
[50662-24-3] **$C_5H_{15}LiTi.2C_{10}H_8N_2$**



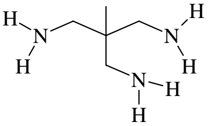
Houben-Weyl, 1975, Vol. 13.3, 288
Friction-sensitive, it decomposes explosively.
See related ALKYLMETALS

†2037. Dimethylaminotrimethylsilane
[2083-91-2] **$C_5H_{15}NSi$**



Xenon difluoride
See Xenon difluoride: Silicon—nitrogen compounds
See related ALKYLSILANES

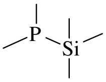
2038. 1,1,1-Tris(aminomethyl)ethane
[15995-42-3] **$C_5H_{15}N_3$**



Preparative hazard

See 1,1,1-Tris(azidomethyl)ethane: Hydrogen, etc.

2039. Dimethyltrimethylsilylphosphine
[26464-99-3] **$C_5H_{15}PSi$**



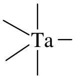
Air, or Water

Goldsberry, R. *et al., Inorg. Chem.*, 1972, **13**, 29—32

It ignites in air and is hydrolysed to dimethylphosphine, also spontaneously flammable.

See related ALKYLPHOSPHINES, ALKYLSILANES

2040. Pentamethyltantalum
[53378-72-6] **$C_5H_{15}Ta$**

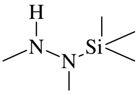


Mertis, K. *et al., J. Organomet. Chem.*, 1975, **97**, C65

It should be handled with extreme caution, even in absence of air, because dangerous explosions have occurred on warming frozen samples or during transfer operations.

See other ALKYLMETALS

2041. 1,2-Dimethyl-2-trimethylsilylhydrazine
[13271-93-7] **$C_5H_{16}N_2Si$**

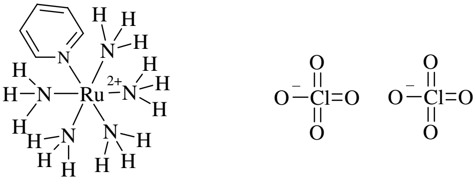


Oxidants

See entry SILYLHYDRAZINES

2042. Pentaamminepyridineruthenium(II) perchlorate

[19482-31-6] **$C_5H_{20}Cl_2N_6O_8Ru$**



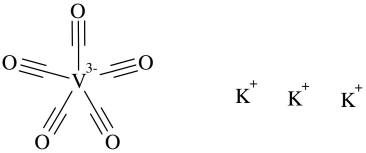
Creutz, C. A., private comm., 1969

The dry salt exploded on touching.

See other AMMINEMETAL OXOSALTS

2043. Potassium pentacarbonylvanadate(3—)

[78937-14-1] **$C_5K_3O_5V$**



Alone, or Poly(chlorotrifluoroethylene)

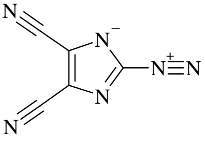
Ellis, J. E. *et al., J. Amer. Chem. Soc.*, 1981, **103**, 6101

It is a pyrophoric and treacherously shock-sensitive explosive, especially as the dry black form. It will deflagrate under nitrogen or argon when scratched with a spatula, and ignites in contact with poly(chlorotrifluoroethylene), (Fluorolube). The caesium and rubidium salts are not shock-sensitive but will deflagrate on friction and are pyrophoric. An insoluble by-product from the preparation will explode if treated with limited amounts of water or alcohol.

See related CARBONYLMETALS

2044. 2-Diazonio-4,5-dicyanoimidazolide (Diazodicyanoimidazole)

[40953-35-3] **C_5N_6**

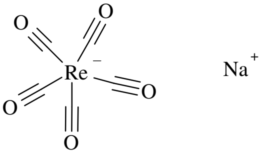


1. Sheppard, W. A. *et al., J. Amer. Chem. Soc.*, 1973, **95**, 2696
2. Sheppard, W. A. *et al., J. Org. Chem.*, 1979, **44**, 1718

It is highly shock-sensitive when dry and explodes above 150°C [1]. It must not be scraped or rubbed, or used in above 2 g portions. The crystalline 1:1 complex with 18-crown-6 ether is significantly less hazardous [2].

See other CYANO COMPOUNDS, DIAZONIUM SALTS, HIGH-NITROGEN COMPOUNDS

2045. Sodium pentacarbonylrhenate
[33634-75-2] **C_5NaO_5Re**

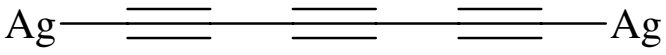


Bailar, 1973, Vol. 3, 955

This and other alkali-metal salts are pyrophoric.

See related CARBONYLMETALS

2046. Silver 1,3,5-hexatriynide
[ ] **C_6Ag_2**

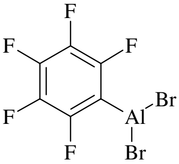


Hunsman, W., *Chem. Ber.*, 1950, **83**, 216

The silver salt may be handled moist, but when dry it explodes violently on touching with a glass rod.

See other METAL ACETYLIDES, SILVER COMPOUNDS

2047. Pentafluorophenylaluminium dibromide
[4457-90-3] **$C_6AlBr_2F_5$**



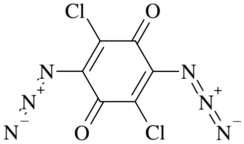
Air, or Water

1. Chambers, R. D. *et al., J. Chem. Soc. (C)*, 1967, 2185
2. Chambers, R. D. *et al., Tetrahedron Lett.*, 1965, 2389

It ignites in air [1], and explodes violently on rapid heating to 195°C or during uncontrolled hydrolysis [2].

See other HALO-ARYLMETALS

2048a. 2,5-Diazido-3,6-dichlorobenzoquinone
[26157-96-0] **$C_6Cl_2N_6O_2$**



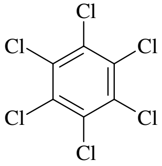
1. Gilligan, W. H., *Tetrahedron Lett.*, 1978, 1676
2. Winkelman, E., *Tetrahedron*, 1969, **25**, 2427

While it does not explode on heating, it is moderately impact-sensitive [1], contradicting an earlier report [2] of absence of explosive properties.

See other 2-AZIDOCARBONYL COMPOUNDS

2048b. Hexachlorobenzene (Perchlorobenzene)

[118-74-1] **C_6Cl_6**

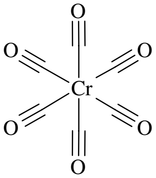


Calcium hydride

See Calcium hydride: Hexachlorobenzene

2049. Hexacarbonylchromium

[13007-92-6] **C_6CrO_6**



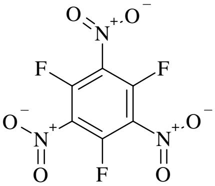
Weast, 1972, B-83

It explodes at 210°C.

See other CARBONYLMETALS

2050a. 1,3,5-Trifluorotrinitrobenzene

[1423-11-6] **$C_6F_3N_3O_6$**



Nucleophiles

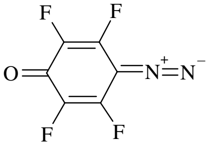
Koppes, W. M. *et al., J. Chem. Soc., Perkin Trans. 1*, 1981, 1817

The title compound readily undergoes substitution reactions with a variety of N, O, C and X nucleophiles. Many of the products of such reactions, especially with hydrazine and its derivatives, are explosive.

See other POLYNITROARYL COMPOUNDS

2050b. 2,3,5,6-Tetrafluoro-1-oxo-4-diazocyclohexa-2,5-diene (2,3,5,6-Tetrafluorobenzenediazonium-4-oxide)

[31438-93-4] **$C_6F_4N_2O$**



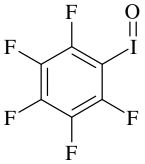
Sander, W. *et al., Chem., Eur. J.*, 2000, **6**(24), 4567

It melts at 65°C with explosive decomposition. It explodes under pressure or on disturbance with metal tools.

ARENEDIAZONIUM OXIDES

2051. Pentafluoroiodosylbenzene

[14353-90-3] **C_6F_5IO**



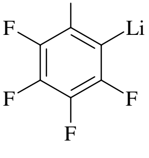
1. Collmann, J. P., *Chem. Eng. News*, 1985, **63**(11), 2
2. Groves, J. T. *et al., Chirality*, 1998, **10**, 106

A 12 g sample decomposed explosively on heating under vacuum at 60°C, though it has been described as stable up to 210°C when it decomposes violently. Avoid heating it to remove volatile impurities [1]. In later safety warnings it has been described as able to detonate spontaneously [2].

See other IODINE COMPOUNDS

2052. Pentafluorophenyllithium

[1076-44-4] **C_6F_5Li**



1. Chernega, A. N. *et al., J. Chem. Soc., Dalt. Trans.*, 1997, (13), 2293
2. Krafft, T. E. USA Pat. 5,679,289, 1996

Pentafluorophenyllithium, obtained as a suspension, detonated above —20°C [1]. A procedure is described for safe preparation and use of this compound in bulk. It depends upon keeping inventories low [2].

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

Deuterium oxide

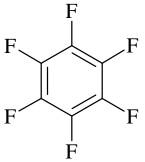
Kinsella, E. *et al., Chem. & Ind.*, 1971, 1017

During addition of an ethereal solution of deuterium oxide (containing some peroxide) to a suspension of the organolithium reagent in pentane, a violent explosion occurred. This may have been initiated by the peroxide present, but probably involved elimination of lithium fluoride.

See other FLUORINATED ORGANOLITHIUM COMPOUNDS, HALO-ARYLMETALS

†2053a. Hexafluorobenzene

[392-56-3] **C_6F_6**



Metals

See HALOARENEMETAL π-COMPLEXES

Silane

Koga, Y. *et al., J. Phys. Chem.*, 1987, **91**(2), 298—305

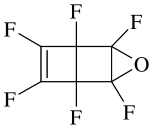
Reaction of hexafluorobenzene and silane under single pulse irradiation of a MW CO_2 laser was explosive.

See other IRRADIATION DECOMPOSITION INCIDENTS

2053b. Hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene

(2,3-Epoxybicyclo[2,2,0]hex-5-ene)

[74415-68-2] **C_6F_6O**



Aluminium chloride

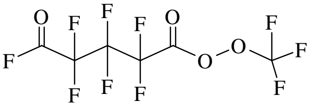
Barlow, M. G. *et al., J. Fluor. Chem.*, 1993, **61**(1-2), 17

A mixture of the two at liquid nitrogen temperature explodes violently on warming to room temperature. Presumably similar behaviour would be experienced with other acids, both Lewis and Bronsted, and quite possibly with some nucleophiles, for the oxaheptene is highly stressed.

STRAINED-RING COMPOUNDS

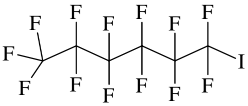
See other 1,2-EPOXIDES

2054. Trifluoromethyl 3-fluorocarbonylhexafluoroperoxybutyrate
[32750-98-4] **$C_6F_{10}O_4$**



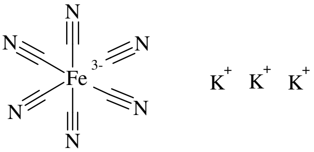
Bernstein, P. A. *et al., J. Amer. Chem. Soc.*, 1971, **93**, 3885
A small sample exploded at 70°C.
See other PEROXYESTERS

2055. Perfluorohexyl iodide
[355-43-1] **$C_6F_{13}I$**



Sodium
See Sodium: Halocarbons (reference 6)

2056. Potassium hexacyanoferrate(III) (‘Potassium ferricyanide’)
[13746-66-2] **$C_6FeK_3N_6$**



HCS 1980, 765

Ammonia
1. Pieters, 1957, 30
2. Sidgwick, 1950, 1359

Contact may be explosive [1], possibly owing to rapid oxidation of ammonia by alkaline ‘ferricyanide’ [2].
See Potassium tetracyanomercurate(II)
See other AMINATION INCIDENTS

Chromium trioxide
See Chromium trioxide: Potassium hexacyanoferrate(III)

Hydrochloric acid
Ephraim, 1939, 303
Treatment of the complex salt with acid liberates the corresponding complex ferricyanic acid, an oxidant which is rather endothermic (ΔH_f° (aq) +640.5 kJ/mol, 2.96 kJ/g), and which forms solid complexes with ether, etc.

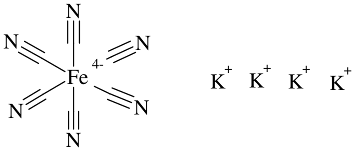
Sodium nitrite

See Sodium nitrite: Metal cyanides

See other METAL CYANIDES (AND CYANO COMPLEXES)

2057. Potassium hexacyanoferrate(II) ('Potassium ferrocyanide')

[13943-58-3] **$C_6FeK_4N_6$**



HCS 1980, 766

Copper(II) nitrate

See Copper(II) nitrate: Potassium hexacyanoferrate(II)

Hydrochloric acid

Ephraim, 1939, 303

Treatment of the complex salt with acid produces the corresponding complex ferrocyanic acid, which is rather endothermic (ΔH_f° (aq) +534.7 kJ/mol, 2.48 kJ/g), and which forms solid complexes with ether, etc.

See other ENDOTHERMIC COMPOUNDS

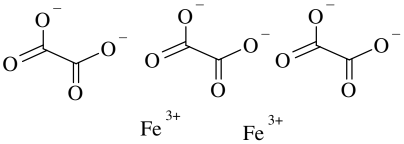
Sodium nitrite

See Sodium nitrite: Metal cyanides

See other METAL CYANIDES (AND CYANO COMPLEXES)

2058. Iron(III) oxalate

[2944-66-3] **$C_6Fe_2O_{12}$**



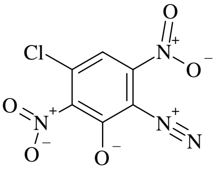
Weinland, R. *et al., Z. Anorg. Chem.*, 1929, **178**, 219

The salt, probably complex, decomposes at 100°C.

See other METAL OXALATES

2059. 4-Chloro-2,5-dinitrobenzenediazonium 6-oxide

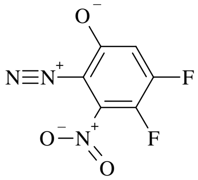
[ ] **$C_6HClN_4O_5$**



See Nitric acid: 4-Chloro-2-nitroaniline
See other ARENEDIAZONIUM OXIDES

2060. 3,4-Difluoro-2-nitrobenzenediazonium 6-oxide

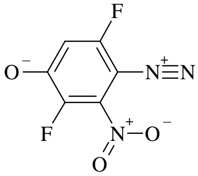
[ ] **$C_6HF_2N_3O_3$**



Finger, G. C. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 148
Diazotisation of 3,4,6-trifluoro-2-nitroaniline under differing conditions gave either this isomer or the 3,6-difluoro 4-oxide (next below), both of which exploded on heating, ignition or impact.
See other ARENEDIAZONIUM OXIDES

2061. 3,6-Difluoro-2-nitrobenzenediazonium 4-oxide

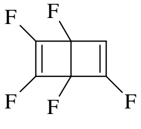
[ ] **$C_6HF_2N_3O_3$**



Finger, G. C. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 148
Diazotisation of 3,4,6-trifluoro-2-nitroaniline under differing conditions gave either this isomer or the 3,4-difluoro 6-oxide (next above), both of which exploded on heating, ignition or impact.
See other ARENEDIAZONIUM OXIDES

2062. 1,2,3,-4,5-Pentafluorobicyclo[2.2.0]hexa-2,5-diene

[21892-31-9] **C_6HF_5**

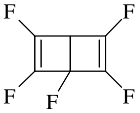


1. Rotajezak, E., *Roczn. Chem.*, 1970, **44**, 447—449
2. Widmann, G. *et al., Thermochim. Acta*, 1988, **134**, 451—455

Both isomers were stored as frozen solids, for as liquids they are more explosive than the hexafluoro ‘Dewar benzene’ analogue [1]. Energy of decomposition (320—540°C) was determined by DSC as 4.60 kJ/g.
See other HALOALKENES, STRAINED-RING COMPOUNDS

2063. 1,2,3,-5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene

[28663-71-0] **C_6HF_5**

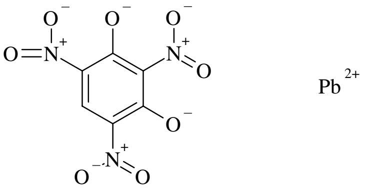


1. Rotajezak, E., *Roczn. Chem.*, 1970, **44**, 447—449
2. Widmann, G. *et al., Thermochim. Acta*, 1988, **134**, 451—455

Both isomers were stored as frozen solids, for as liquids they are more explosive than the hexafluoro ‘Dewar benzene’ analogue [1]. Energy of decomposition (320—540°C) was determined by DSC as 4.60 kJ/g.
See other HALOALKENES, STRAINED-RING COMPOUNDS

2064. Lead 2,4,6-trinitroresorcinoxide (‘Lead styphnate’)

[15245-44-0] **$C_6HN_3O_8Pb$**

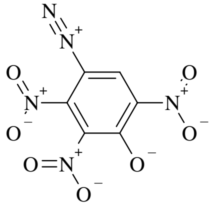


1. *MCA Case History No. 957*
2. Okazaki, K. *et al., Chem. Abs.*, 1977, **86**, 57638
3. Biasutti, 1981, 63, 73, 75, 86, 108

Three beakers containing lead styphnate were being heated in a laboratory oven to dry the explosive salt. When one of the beakers was moved, all 3 detonated. Other heavy metal salts of polynitrophenols are dangerously explosive when dry [1]. The desensitising effect of presence of water upon the friction sensitivity of this priming explosive was studied. There is no effect up to 2% content and little at 5%. Even at 20% water content it is still as sensitive as dry pentaerythritol tetranitrate [2]. In one incident in 1927, 20 kg of the dry salt exploded while being poured into paper bags. Initiation by static sparks in a very dry atmosphere was supposed. In another incident, 1 kg exploded during drying in thin layers in an oven held below 65°C. In a third incident, sifting of the dry material also led to the explosion of adjacent wet material, though in a fourth incident, the latter did not also explode. The other incidents involved explosions during drying or handling operations [3].

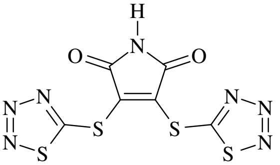
See LEAD SALTS OF NITRO COMPOUNDS
See other HEAVY METAL DERIVATIVES, METAL NITROPHENOXIDES, POLYNITROARYL COMPOUNDS

2065. 2,3,5-Trinitrobenzenediazonium-4-oxide
[91144-94-4] **$C_6HN_5O_7$**



Meldola, R. *et al., J. Chem. Soc.*, 1909, **95**, 1383
It is extremely explosive.
See other ARENEDIAZONIUM OXIDES

2066. 3,4-Bis(1,2,3,4-thiatriazol-5-ylthio)maleimide
[1656-16-2] **$C_6HN_7O_2S_4$**



Pilgram, K. *et al., Angew. Chem.*, 1965, **77**, 348
This compound of low oxygen balance explodes loudly on impact or at the m.p.
See other HIGH-NITROGEN COMPOUNDS, N—S COMPOUNDS

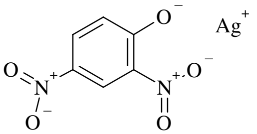
2067. 1,3,5-Hexatriyne
[3161-99-7] **C_6H_2**

1. Hunsman, W., *Chem. Ber.*, 1950, **83**, 213—217
2. Armitage, J. B. *et al., J. Chem. Soc.*, 1952, 2013
3. Bjornov, E. *et al., Spectrochim. Acta*, 1974, **30A**, 1255—1256

It polymerises slowly at —20°C, but rapidly at ambient temperature in air to give a friction-sensitive explosive solid, probably a peroxide [1]. Although stable under vacuum at —5°C for a limited period, exposure at 0°C to air led to violent explosions soon afterwards [2]. Explosive hazards have again been stressed [3].
See other ALKYNES

2068. Silver 2-azido-4,6-dinitrophenoxide

[82177-80-8] **$C_6H_2AgN_5O_5$**



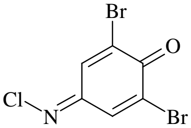
Spear, R. J. *et al., Aust. J. Chem.*, 1982, **35**, 5

Of a series of 17 compounds examined as stab-initiation sensitisers, the title compound had the lowest ignition temperature of 122°C.

See other METAL NITROPHENOXIDES, ORGANIC AZIDES, POLYNITROARYL COMPOUNDS, SILVER COMPOUNDS

2069. 2,6-Dibromobenzoquinone-4-chloroimide

[537-45-1] **$C_6H_2Br_2ClNO$**



1. Hartmann, W. W. *et al., Org. Synth.*, 1943, Coll. Vol. 2, 177
2. Horber, D. F. *et al., Chem. & Ind.*, 1967, 1551
3. Taranto, B. J., *Chem. Eng. News*, 1967, **45**(24), 54

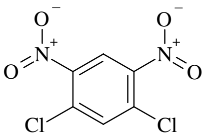
The chloroimide decomposed violently on a drying tray at 60°C [1], and a bottle accidentally heated to 50°C exploded [2]. Decomposition of the heated solid occurs after a temperature-dependent induction period. Unheated material eventually exploded after storage at ambient temperature [3].

See 2,6-Dichlorobenzoquinone-4-chloroimide

See other *N*-HALOGEN COMPOUNDS, INDUCTION PERIOD INCIDENTS

2070. 1,5-Dichloro-2,4-dinitrobenzene

[3698-83-7] **$C_6H_2Cl_2N_2O_4$**



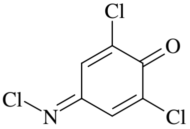
Dimethyl sulfoxide, Potassium fluoride

Koch-Light Laboratories Ltd., private comm., 1976

A mixture of the (highly activated) dichloro compound with potassium fluoride in the solvent was heated to reflux to effect replacement of chlorine by fluorine. The reaction accelerated out of control and exploded, leaving much carbonised residue. Analogous reactions had been effected uneventfully on many previous occasions.

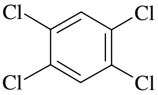
See Dimethyl sulfoxide: Acyl halides, etc.
See other HALOARYL COMPOUNDS, POLYNITROARYL COMPOUNDS

2071. 2,6-Dichlorobenzoquinone-4-chloroimide
[101-38-2] **$C_6H_2Cl_3NO$**



Taranto, B. J., *Chem. Eng. News*, 1967, **45**(52), 54
The heated solid material decomposed violently after a temperature-dependent induction period. Unheated material eventually exploded after storage at ambient temperature.
See 2,6-Dibromobenzoquinone-4-chloroimide
See other *N*-HALOGEN COMPOUNDS, INDUCTION PERIOD INCIDENTS

2072. 1,2,4,5-Tetrachlorobenzene
[95-94-3] **$C_6H_2Cl_4$**



Sodium hydroxide, Solvent

1. Anon., *Chem. Eng. News*, 1983, **61**(23), 44
2. *MCA Case History No. 620*
3. Hofmann, H. T., *Arch. exptl. Pathol. Pharmakol.*, 1957, **232**, 228—230
4. Cardillo, P. *et al., J. Haz. Mat.*, 1984, **9**, 221—234
5. Sambeth, J. A., *Chimia*, 1982, **36**, 128—132
6. Anon., *ABCM Quart. Safety Summ.*, 1952, **23**, 5
7. May, G., *Brit. J. Ind. Med.*, 1973, **30**, 276—277
8. Milnes, M. H., *Nature*, 1971, **232**, 396
9. Calnan, A. B., private comm., 1972
10. Theofanous, T. G., Statement at special meeting of Society of Chemical Industry's Industrial Health & Safety Group, London, 23rd March, 1981; *Chem. & Ind.*, 1981, 197; *Nature*, 1981, **291**, 640
11. Theofanous, T. G., *Chem. Engrg. Sci.*, 1983, **38**, 1615
12. Salomon, C. M., *Chimia*, 1982, **36**, 133—139
13. Künzi, H., *Chimia*, 1982, **36**, 162—168
14. Cardillo, P. *et al., Chim. e Ind.* (Milan), 1983, **65**, 611—615
15. Theofanous, T. G., *Chem. Engrg. Sci.*, 1983, **38**, 1631
16. Cardillo, P. *et al., Chim. e Ind. (Milan)*, 1982, **64**, 781—784
17. Marshall, V. C., *Loss Prevention Bull.*, 1992, **104**, 15
18. Gustin, J.-L., *Trans. Inst. Chem. Eng*, 2002, **80**(B), 16

Eight serious accidents occurred during the commercial preparation of 2,4,5-trichlorophenol by alkaline partial hydrolysis of 1,2,4,5-tetrachlorobenzene during the period 1949 to 1976 [1], involving two distinct processes, each with their particular potential hazards. The earlier process used methanolic alkali under autogenous pressure to effect the hydrolysis, and on 2 occasions around 1949 the reaction at 125°C went out of control, one attaining 400°C [2]. One of the principal hazards of this pressurised process is associated with the fact that no reflux is possible, so the reaction exotherm must be removed by applied cooling in a batch reactor, (or by controlled flow rate in a continuous reactor) to prevent undue temperature rise. A second potential hazard resides in the fact that if the sodium hydroxide normally used as base (and in excess) is not completely dissolved in the methanol before the temperature of onset of hydrolysis (165—180°C) is reached, the hydrolysis exotherm (108.4 kJ/mol of tetrachlorobenzene) is increased by the solution exotherm (perhaps 30—90 kJ/mol) of undissolved alkali, and a runaway reaction, accompanied by a rapid and uncontrollable pressure increase may develop. In a further incident in 1953, the explosion was associated with the post-reaction stage during distillation of methanol from the reaction mixture [3]. Under these conditions a virtually solid crust of the sodium phenoxide is formed and may become overheated [4]. Four explosions occurred during the commercial use of the methanol process [5].

The later process used ethylene glycol as solvent to effect hydrolysis with sodium hydroxide and operated essentially at or near atmospheric pressure. Hydrolysis was effected at between 140 and 180°C during several hours, and the excess glycol (that portion which did not condense to relatively involatile diethylene glycol) might or might not be recovered by vacuum distillation, depending on the process design. When another solvent was present in the reaction system (dichlorobenzene to dissolve sublimed tetrachlorobenzene from the condenser in the Coalite system, or xylene to assist in water and glycol removal in the Seveso system), some inherent temperature control by reflux during the hydrolysis reaction was possible. Violent decomposition could, however, occur during the subsequent solvent distillation phase in the absence of effective temperature control. A laboratory residue from vacuum stripping using electric heating (without knowledge of the liquid temperature) exploded when the vapour temperature had reached 160°C [6]. In the Coalite plant incident in 1968, where the hydrolysis was run at about 180°C in a reaction vessel heated by circulating oil at 300°C, failure of the manually regulated oil heating system led to an uncontrollable temperature increase during 50 m to above 250°C, when a violent explosion occurred [7]. Subsequent work showed that an accelerating exothermic decomposition sets in at 230°C, capable of attaining 410°C. This involves sodium hydroxide and ethylene glycol (or diethylene glycol) and produces hydrogen, thus pressurisation, and sodium carbonate [8,16].

The Seveso accident in 1976 also involved the glycol-based process, but differed fundamentally from the 1968 incident. While the latter apparently involved a thermal runaway initiated during the hydrolysis reaction by application of excessive heat by the faulty hot oil system [7], the process design adopted by Icmesa at Seveso featured heating the reaction vessel by steam at 12 bar (192°C if saturated) to ensure a minimum 40°C safety margin below the known decomposition temperature of 230°C [5]. At Seveso the exothermic hydrolysis reaction had been completed, but not the ensuing xylene—glycol solvent distillation, before the weekend shutdown, when the liquid temperature was 158°C. The bursting disk set at 3.8 bar failed some 7.5 h after processing operations, agitation and heating had been terminated [5]. The accident was followed by an unprecedented amount of investigational work; giving a highly probable explanation if several factors and new information are taken into account.

It was found that the steam supply to the reactor was often superheated (just prior to shutdown to 330°C) [10]. Although this degree of superheat would not grossly increase the temperature of the inner reactor wall in contact with the liquid (or the bulk liquid temperature) [11], it seems probable that any reaction material splashed onto and dried out at the top of the coil-heated wall would have become heated to a much higher temperature. Further detailed work on the thermal stability of the mixture showed that a previously unsuspected very slow exothermic decomposition existed, beginning at 180°C and proceeding at an appreciable rate only above 200°C, so that the exotherm was insufficient to heat the contents of the reactor from the last recorded temperature of 158°C to the decomposition temperature of 230°C in 7.5 h [12,13,14]. It was concluded that an alternative (effectively an external) source of heat was necessary to account for the observed effect, and the residual superheat from the steam at 330°C seems to have been that source.

Any superheating effect would be localised near the steam inlet at the top of the vessel, and there would not have been enough excess heat to raise the temperature of the whole reactor contents by more than a few °C. A new physicochemical process involving conduction, convection and radiation was proposed, and verified experimentally, which concentrated the available excess heat into the top surface layer of a few cm (a few % of the total depth) of the reactor contents, so that the critical temperature of 230°C would be attained in that top layer [11]. The exothermic decomposition reaction, (perhaps catalysed by any thermal degradation products falling into the top layer from the overheated top of the reactor) would then have propagated rapidly downwards into the reactor contents (some 6 t), leading to runaway reaction, pressure build-up and bursting disk failure with release of the reactor contents to atmosphere [11,15]. It has later been claimed that, the sodium hydroxide glycol reaction starting below 200°C given sufficiently long initiation period, no external heat was needed [18].

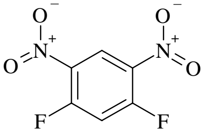
A publication summarises all the then available technical evidence related to the Seveso accident, and recommends operational criteria to ensure safety in commercial processes to produce trichlorophenol [4]. All the plant scale incidents were characterised [1] by the subsequent occurrence of chloracne arising from the extremely toxic and dermatitic compound 2,3,7,8-tetrachlorodibenzodioxin, formed during the thermal runaway reaction and dispersed in the ensuing explosion. It is also extremely resistant to normal chemical decontamination procedures, and after the 1968 explosion, further cases occurred after transient contact with plant which had been decontaminated and allowed to weather for 3 years, and which appeared free of ‘dioxin’ [7,9]. The consequences at Seveso: 447 cases of chemical burns (NaOH); and 179 of chloracne, only 34 with both [17].

See Sodium hydroxide: Glycols

See other GAS EVOLUTION INCIDENTS, HALOARYL COMPOUNDS, RUNAWAY REACTIONS

2073. 1,5-Difluoro-2,4-dinitrobenzene

[327-92-4] $C_6H_2F_2N_2O_4$



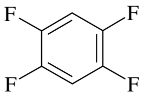
Preparative hazard

See 1,5-Dichloro-2,4-dinitrobenzene: Dimethyl sulfoxide, etc.

See other HALOARYL COMPOUNDS, POLYNITROARYL COMPOUNDS

†2074. 1,2,4,5-Tetrafluorobenzene

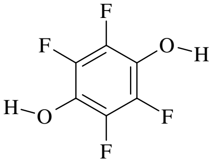
[327-54-8] $C_6H_2F_4$



See other HALOARYL COMPOUNDS

2075. Tetrafluorobenzene-1,4-diol

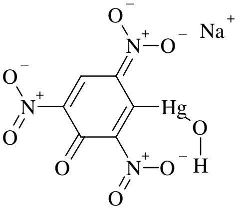
[771-63-1] $C_6H_2F_4O_2$



See Trimethylaluminium: Tetrafluorobenzene-1,4-diol

2076. Sodium 3-hydroxymercurio-2,6-dinitro-4-*aci*-nitro-2,5-cyclohexadienonide

[ ] $C_6H_2HgN_3NaO_5$

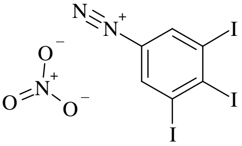


Hantzsch, A. *et al., Ber.*, 1906, **39**, 1111

This salt of the mono-*aci* *p*-quinonoid form of 3-hydroxymercurio-2,4,6-trinitrophenol explodes on rapid heating.

See entry aci-NITROQUINONOID COMPOUNDS

2077. 3,4,5-Triiodobenzenediazonium nitrate
[68596-99-6] **$C_6H_2I_3N_3O_3$**

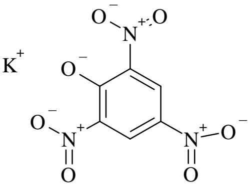


Kalb, L. *et al., Ber.*, 1926, **59**, 1867

Unstable on warming, explodes on heating in a flame.

See other DIAZONIUM SALTS

2078. Potassium picrate (Potassium 2,4,6-trinitrophenoxide)
[573-83-1] **$C_6H_2KNO_7$**

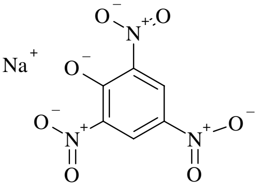


2,2-Dinitro-2-fluoroethoxycarbonyl chloride

See 2,2-Dinitro-2-fluoroethoxycarbonyl chloride: Potassium picrate

See other PICRATES

2079. Sodium picrate (Sodium 2,4,6-trinitrophenoxide)
[73771-13-8] **$C_6H_2N_3NaO_7$**

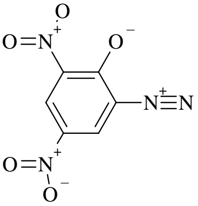


1. Coningham, H., *H. M. Insp. Expl. Rept. 236*, London, 1919
2. Nakagawa, K. *et al., Bull. Chem. Soc. Japan*, 1987, **60**, 2038, footnote

A large scale explosion involving initiation of wet sodium picrate by impact was investigated [1]. A small sample heated to above 250°C exploded with sufficient violence to destroy the DTA thermocouple [2].

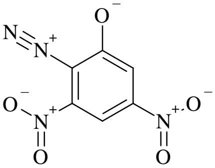
See other METAL NITROPHENOXIDES, PICRATES

2080. 3,5-Dinitrobenzenediazonium 2-oxide (5,7-Dinitrobenzoxa-1,2,3-diazole)
[4682-03-5] [87-31-0] (oxadiazole form) **$C_6H_2N_4O_5$**



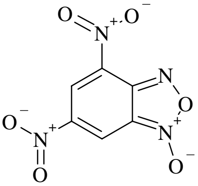
It appears uncertain which structure this explosive has, quite possibly both, since it can be made either by diazotisation or nucleophilic cyclisation.
See N,2,3,5-Tetranitroaniline
See other ARENEDIAZONIUM OXIDES

2081. 4,6-Dinitrobenzenediazonium 2-oxide
[ ] **$C_6H_2N_4O_5$**



Urbanski, 1967, Vol. 3, 204
This priming explosive, as sensitive as mercury fulminate, is much more powerful than metal-containing initiators.
See other ARENEDIAZONIUM OXIDES

2082. 4,6-Dinitrobenzofurazan *N*-oxide
[5128-28-9] **$C_6H_2N_4O_6$**



Norris, W. P. *et al., Aust. J. Chem.*, 1983, **36**, 306
A powerful high explosive, of comparable sensitivity to dry picric acid.

Cysteine
See 4-(2'-Ammonio-2'-carboxyethylthio)-5,7-dinitro-4,5-dihydro-benzofurazanide *N*-oxide

Furan, or *N*-Methylindole, or *N*-Methylpyrrole

Halle, J. C. *et al., Tetrahedron Lett.*, 1983, **24**, 2258

The mono- or bis-furoxan adducts are explosive, and work on them was discontinued.

Ketones

Terrier, F. *et al., J. Org. Chem.*, 1981, **46**, 3538

The adducts formed with acetone, cyclopentanone, cyclopentanedione, 2,4-pentanedione or 3-methyl-2,4-pentanedione form insoluble potassium salts (M = K), but these are highly explosive and shock-sensitive and should not be isolated, but handled only in solution.

Nucleophilic reagents

1. Norris, W. P. *et al., Aust. J. Chem.*, 1983, **36**, 297—309
2. Boga, C. *et al., J. Chem. Soc. Perk. I*, 2001 (8), 1408

Reaction of the title compound with a series of nucleophilic oxygen reagents (potassium hydrogencarbonate in water or methanol, potassium hydroxide in methanol), or nitrogen reagents (ammonia, hydroxylamine or hydrazine hydrate) gives a series of mono- or binuclear 7-substituted Meisenheimer complexes. All of these are explosives sensitive to initiation by impact, friction or electrostatic discharge, which need due care in handling [1]. The potassium hydroxide adduct has its own entry. A further study of Meisenheimer complexes with a variety of secondary and tertiary amines (piperidine, quinuclidine and diazabicyclo- octane and nonene) warns that these too are explosive [2].

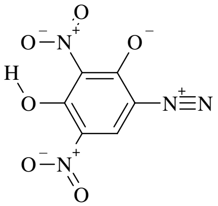
See Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide

See also 4-Nitrobenzofurazan 1-oxide

See other FURAZAN N-OXIDES, POLYNITROARYL COMPOUNDS

2083. 3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide

[29906-35-2] **$C_6H_2N_4O_6$**



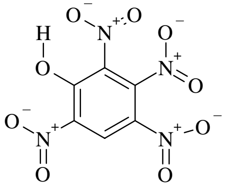
Dynamit Nobel, Belg. Pat. 874 187, 1979

The barium, lead and potassium salts (on the 4-position) are sensitive detonators.

See other ARENEDIAZONIUM OXIDES, POLYNITROARYL COMPOUNDS

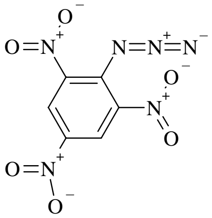
2084. 2,3,4,6-Tetranitrophenol

[641-16-7] **$C_6H_4N_2O_9$**



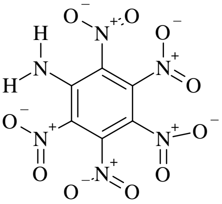
Sorbe, 1968, 152
Exceptionally explosive.
See other POLYNITROARYL COMPOUNDS

2085. Picryl azide (2,4,6-Trinitrophenyl azide)
[1600-31-3] **$C_6H_2N_6O_6$**



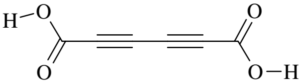
Schrader, E., *Ber.*, 1917, **50**, 778
Explodes weakly under impact, but not on heating.
See other ORGANIC AZIDES, POLYNITROARYL COMPOUNDS

2086. Pentanitroaniline
[21985-87-5] **$C_6H_2N_6O_{10}$**



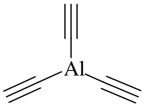
Koppes, W. M. *et al., J. Chem. Soc., Perkin Trans. 1*, 1981, 1816
It is a very sensitive explosive.
See other POLYNITROARYL COMPOUNDS

2087. 2,4-Hexadiyne-1,6-dioic acid
[1072-17-9] **$C_6H_2O_4$**



Sorbe, 1968, 109
Explodes on heating.
See other ACETYLENIC COMPOUNDS, ORGANIC ACIDS

2088. Triethynylaluminium
[61204-16-8] **C_6H_3Al**



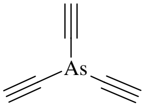
Diethyl ether, or Dioxane, or Trimethylamine

1. Chini, P. *et al., Chim. e Ind.* (Milan), 1962, **44**, 1220
2. Houben-Weyl, 1970, Vol. 13.4, 159

The residue from sublimation of the complex with dioxane is explosive, and the complex should not be dried by heating. The trimethylamine complex may also explode on sublimation [1]. Triethynylaluminium or its complex with diethyl ether may decompose explosively on heating. Sublimation is not therefore advised as a purification method [2].

See other METAL ACETYLIDES

2089. Triethynylarsine
[687-78-5] **C_6H_3As**

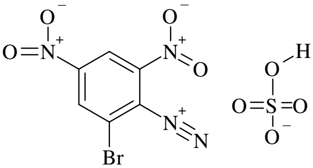


Voskuil, W. *et al., Rec. Trav. Chim.*, 1964, **83**, 1301

It explodes on strong friction.

See related METAL ACETYLIDES

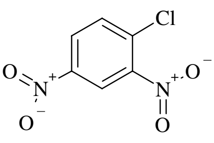
2090. 6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate
[65036-47-7] **$C_6H_3BrN_4O_8S$**



See entry DIAZONIUM SULFATES

See other POLYNITROARYL COMPOUNDS

2091. 1-Chloro-2,4-dinitrobenzene
[97-00-7] **$C_6H_3ClN_2O_4$**



HCS 1980, 299

Sorbe, 1968, 56

T_{ait24} was determined as 250°C by adiabatic Dewar tests, with an apparent energy of activation of 185 kJ/mol.

It has been used as an explosive.

See 1-Fluoro-2,4-dinitrobenzene

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Ammonia

1. Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389—390
2. Wells, F. B. *et al., Org. Synth.*, 1943, Coll. Vol. 2, 221—222

During the preparation of 2,4-dinitroaniline by a well-established procedure involving heating the reactants in a direct-fired autoclave (170°C and 40 bar were typical conditions), a sudden increase in temperature and pressure preceded a violent explosion [1]. An alternative process avoiding the use of a sealed vessel is now used [2].

See 2-Chloronitrobenzene: Ammonia

See other AMINATION INCIDENTS, POLYNITROARYL COMPOUNDS: Bases, or Salts

Hydrazine hydrate

491M, 1975, 201

In absence of diluent, the reaction is sufficiently exothermic and violent to shatter the flask.

Other reactants

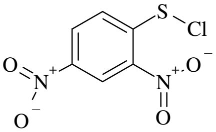
Yoshida, 1980, 157

MRH values calculated for 7 combinations with materials catalysing its decomposition are given.

See other HALOARYL COMPOUNDS, POLYNITROARYL COMPOUNDS

2092. 2,4-Dinitrobenzenesulfenyl chloride

[528-76-7] **$C_6H_3ClN_2O_4S$**



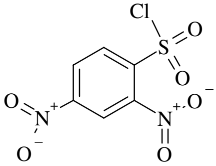
Kharasch, N. *et al., Org. Synth.*, 1964, **44**, 48

During removal of solvent under vacuum, the residual chloride must not be overheated, as it may explode.

See other POLYNITROARYL COMPOUNDS

See related NITROACYL HALIDES

2093. 2,4-Dinitrobenzenesulfonyl chloride
[1656-44-6] **$C_6H_3ClN_2O_6S$**

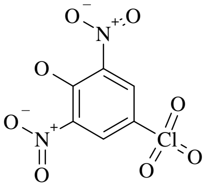


Preparative hazard

See Bis(2,4-dinitrophenyl) disulfide: Chlorine

See other NITROACYL HALIDES, POLYNITROARYL COMPOUNDS

2094. 2,6-Dinitro-4-perchlorylphenol
[89284-66-2] **$C_6H_3ClN_2O_8$**

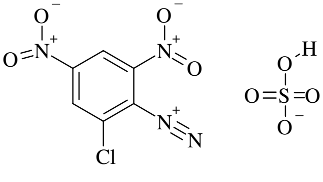


Gardner, D. M. *et al., J. Org. Chem.*, 1963, **28**, 2652

This analogue of picric acid is dangerously explosive and very shock-sensitive.

See other PERCHLORYL COMPOUNDS, POLYNITROARYL COMPOUNDS

2095. 6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate
[68597-05-7] **$C_6H_3ClN_4O_8S$**



See entry DIAZONIUM SULFATES

See other POLYNITROARYL COMPOUNDS

2096. Dichloronitrobenzene
[?] **$C_6H_3Cl_2NO_2$**

$Cl_2C_6H_3NO_2$

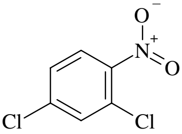
Aniline

Anon., *Chem. Hazards Ind.*, 1992, (Feb.), 171

A reaction with an unspecified isomer of dichloronitrobenzene ran wild on overheating.

See other NITROARYL COMPOUNDS, RUNAWAY REACTIONS

2097. 2,4,-Dichloronitrobenzene
[611-06-3] **$C_6H_3Cl_2NO_2$**



Acetic acid, Potassium fluoride, Dimethylacetamide

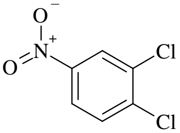
1. Mooney, D. G., *Hazards XI,* 38132, Symp. Ser. 124, Rugby (UK), IChE, 1991
2. van Reijendam, J. W. *et al., J. Loss Prev. Proc. Ind.,* 1992, **5**(4), 211

A Halex process, exchanging the chlorine for fluorine in solvent dimethylacetamide, on 15,000l scale with above a tonne of substrate, showed a runaway exotherm from 160°C, followed by rupture of the vessel and formation of a fireball by the contents. Fragments and damage extended up to 500 m distance. Examination suggested that a complex chain of events, starting with large scale contamination of a previous batch by water during work up, had produced recycled dimethylacetamide contaminated with acetic acid. Acetate then acted as nucleophile, subsequently eliminating ketene to produce a phenol, itself another nucleophile producing diphenyl ethers. The limited exotherm produced by these reactions was enough to take the mix to 250°C, where a more exothermic reaction, probably involving the oxidant nitro group, sets in. Presumably similar reactions could take place with other halonitrobenzenes.

See 5-Fluoro-2-nitrophenol

See other HALOARYL COMPOUNDS, NITROARYL COMPOUNDS, RUNAWAY REACTIONS

2098. 3,4-Dichloronitrobenzene
[99-54-7] **$C_6H_3Cl_2NO_2$**

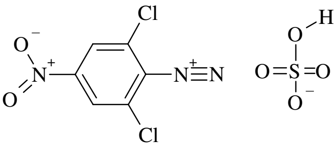


Catalyst, Hydrogen

See 3,4-Dichlorophenylhydroxylamine

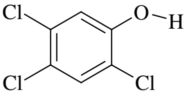
See other HALOARYL COMPOUNDS, NITROARYL COMPOUNDS

2099. 2,6-Dichloro-4-nitrobenzenediazonium hydrogen sulfate
[68597-06-8] **$C_6H_3Cl_2N_3O_6S$**



See entry DIAZONIUM SULFATES

2100. 2,4,5-Trichlorophenol
[95-95-4] **$C_6H_3Cl_3O$**

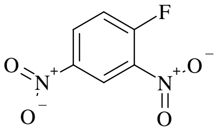


Preparative hazard

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent

See other HALOARYL COMPOUNDS

2101. 1-Fluoro-2,4-dinitrobenzene
[70-34-8] **$C_6H_3FN_2O_4$**



HCS 1980, 505

1. Halpern, B. D., *Chem. Eng. News*, 1951, **29**, 2666
2. Muir, G. D., private comm., 1969
3. Reinheimer, J. D. *et al., J. Amer. Chem. Soc.*, 1961, **83**, 837

The residue left from conversion of the chloro to the fluoro compound exploded during distillation at 1.3 mbar [1]. Reheating the residue from distillation caused violent decomposition [2]. Traces of an *aci*-nitroquinonoid species may have been formed in the chlorodinitrobenzene—potassium fluoride reaction system [3].

See related aci-NITROQUINONOID COMPOUNDS

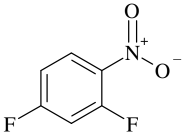
Ether peroxides

Shafer, P. R., private comm., 1967

When air was admitted after vacuum evaporation of a (peroxidic) ether solution of the dinitro compound (5 g), a violent explosion occurred. Exploding ether peroxide may have initiated the dinitro compound.

See other HALOARYL COMPOUNDS, POLYNITROARYL COMPOUNDS

2102. 2,4-Difluoronitrobenzene
[446-35-5] **$C_6H_3F_2NO_2$**



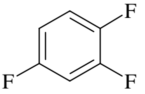
Sodium hydroxide, Dioxane, Water

See 5-Fluoro-2-nitrophenol

See other NITROARYL COMPOUNDS

†2103. 1,2,4-Trifluorobenzene

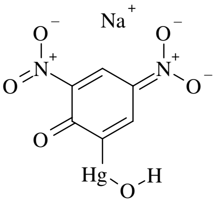
[367-23-7] **$C_6H_3F_3$**



See other HALOARYL COMPOUNDS

2104. Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide

[ ] **$C_6H_3HgN_2NaO_6$**



Hantzsch, A. *et al., Ber.*, 1906, **39**, 1113

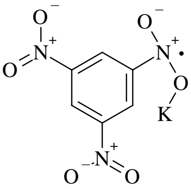
This salt of the mono-*aci*-*p*-quinonoid form of 2-hydroxymercurio-4,6-dinitrophenol explodes violently on strong heating.

See entry aci-NITROQUINONOID COMPOUNDS

See other MERCURY COMPOUNDS, POLYNITROARYL COMPOUNDS

2105. Potassium 1,3,5-trinitrobenzene

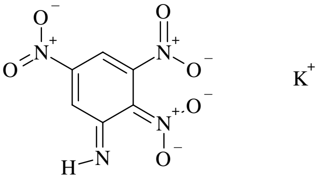
[ ] **$C_6H_3KN_3O_6$**



See entry NITROAROMATIC—ALKALI HAZARDS; Potassium radical salts

2106. Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide

[12244-59-6] (ion) **$C_6H_3KN_4O_6$**



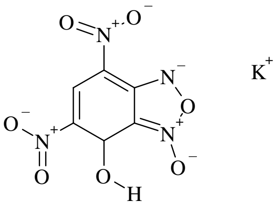
Green, A. G. *et al., J. Chem. Soc.*, 1913, **103**, 508—513

This salt of the *aci-o*-iminoquinonoid form of 2,4,6-trinitroaniline explodes violently at 110°C.

See entry aci-NITROQUINONOID COMPOUNDS

See other POLYNITROARYL COMPOUNDS

2107. Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide
[57891-85-7] (ion) $C_6H_3KN_4O_7$

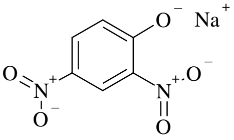


1. Boulton, A. J. *et al., J. Chem. Soc.*, 1965, 5414
2. Spear, R. J., *Aust. J. Chem.*, 1982, **35**, 4
3. Spear, R. J. *et al., Prop. Explos., Pyrotech.*, 1983, **8**, 95—98

The complex formed between 4,6-dinitrobenzofurazan 1-oxide and potassium hydroxide has been evaluated as an explosive [1]. The structure is now believed to be that of a Meisenheimer complex [2]. The analogous sodium, silver and barium salts are also explosive, the latter being less sensitive to initiation [3].

See other FURAZAN N-OXIDES, POLYNITROARYL COMPOUNDS

2108a. Sodium 2,4-dinitrophenoxide
[38892-09-0] $C_6H_3N_2NaO_5$

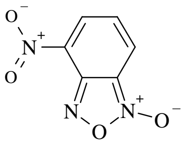


1. Hickson, B., *Chem. Age*, 1926, **14**, 522
2. Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 388—390

A violent explosion occurred during centrifugal dehydration of an aqueous paste of the sodium salt [1], which was known to be explosive [2]. The instability may be associated with the presence of some of the *aci-o-* or *p*-quinonoid salt.

See other METAL NITROPHENOXIDES, NITROAROMATIC—ALKALI HAZARDS, POLYNITROARYL COMPOUNDS

2108b. 4-Nitrobenzofurazan 1-oxide (4-Nitrobenzofuroxan)
[18771-85-2] $C_6H_3N_3O_4$



Boga, C. *et al., J. Chem. Soc., Perk. 2*, 2001, (8), 1408

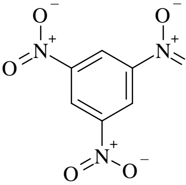
Reaction of this compound, or the considerably more explosive 2,6-dinitrobenzofuroxan, with nucleophiles (secondary and tertiary amines, sodium hydroxide) showed evidence of Meisenheimer type complexes being formed – zwitteionic in the case of tertiary amines. Some of these broke down by elimination of water to give substituted benzoxadiazoles. All complexes and other isolated products are described as explosive.

4,6-Dinitrobenzofurazan *N*-oxide: Nucleophilic reagents

See other FURAZAN N-OXIDES

2109. 1,3,5-Trinitrobenzene

[99-35-4] **$C_6H_3N_3O_6$**



Alkylmetallates, or Arylmetallates

Artamkina, G. M. *et al., J. Organomet. Chem.*, 1979, **182**, 185

The THF-containing complexes formed between trinitrobenzene and the lithium or potassium salts of trimethyl-, triethyl- or triphenyl-germanate, -silanate or -stannate decompose explosively on heating, though trinitrobenzene—potassium trimethylstannate decomposes explosively at ambient temperature.

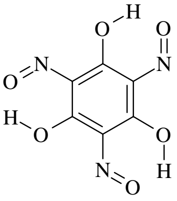
Methanol, Potassium hydroxide

See Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide

See other POLYNITROARYL COMPOUNDS

2110. Trinitrosophloroglucinol (2,4,6-Trinitrosobenzene-1,3,5-triol)

[200002-30-8] **$C_6H_3N_3O_6$**



The isomeric cyclohexanehexone 1,3,5-trioxime is identified as [14378-99-5].

Heavy metal compounds

Heavy metal salts (possibly of the oxime form) may be hazardous.

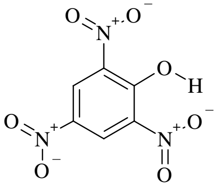
See Lead(II) trinitrosobenzene-1,3,5-trioxide

See other NITROSO COMPOUNDS

See related OXIMES

2111. Picric acid (2,4,6-Trinitrophenol)

[88-89-1] **$C_6H_3N_3O_7$**



NSC 351, 1979; *FPA H128*, 1983; *HCS 1980*, 755; *RSC Lab. Hazards Data Sheet No. 34*, 1985

The first high explosive shock-resistant enough to find use in shells. Most of its salts are more sensitive.

Alone, or Heavy metals, or Bases

1. Cooper-Key, A., *Home Office Rept. 211*, 9, HMSO, 1914
2. Kirk-Othmer, 1965, Vol. 8, 617
3. Urbanski, 1964, Vol. 1, 518
4. Garey, H. E., *Chem. Eng. News*, 1979, **57**(41), 51
5. Ventrone, T. A., *CHAS Notes*, 1982, **1**(3), 1—2; (4), 4
6. Mendenhall, G. D., *Chem. Eng. News*, 2005, **83**(6), 5

Picric acid, in common with several other polynitrophenols, is an explosive material in its own right and is usually stored as a water-wet paste. Several dust explosions of dry material have been reported [1]. It forms salts with many metals, some of which (lead, mercury, copper or zinc) are rather sensitive to heat, friction or impact. The salts with ammonia and amines, and the molecular complexes with aromatic hydrocarbons, etc. are, in general, not so sensitive [2]. Contact of picric acid with concrete floors may form the friction-sensitive calcium salt [3]. Contact of molten picric acid with metallic zinc or lead forms the metal picrates which can detonate the acid. Picrates of lead, iron, zinc, nickel, copper, etc. should be considered dangerously sensitive. Dry picric acid has little effect on these metals at ambient temperature. Picric acid of sufficient purity is of the same order of stability as TNT,and is not considered unduly hazardous in regard to sensitivity [4]. Details of handling and disposal procedures have been collected and summarised [5]. Once a reagent found in most laboratories, it now excites undue fear; in reaction to an ill-informed safety officer's demand for removal or destruction of a bottle of the wet solid, one chemist introduced synthesis and drop-weight detonation tests into a university teaching course. It seldom or never detonated, while dibenzoyl peroxide, sold to the public in concentrated form as a resin hardener, always did. (The safety officiouser was satisfied by a certificate alleging that the wet acid had been converted to perhaps more dangerous dry picryl chloride) [6]. Subsequent editions of the journal are loud with the protests of 'Safety Professionals.'

See Sodium picrate

See also Ammonium picrate

Aluminium, Water

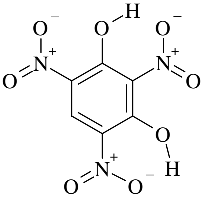
See Aluminium: Nitro compounds, etc.

Uronium perchlorate

See Uronium perchlorate: Organic materials

See other ORGANIC ACIDS, POLYNITROARYL COMPOUNDS

2112. Trinitroresorcinol (2,4,6-Trinitrobenzene-1,3-diol)
[82-71-3] **$C_6H_3N_3O_8$**

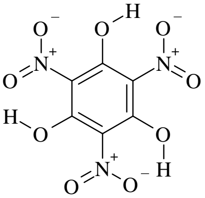


Sorbe, 1968, 152

The compound ('styphnic acid', +6.7% oxygen balance) and its salts are very explosive.

See other ORGANIC ACIDS, POLYNITROARYL COMPOUNDS

2113. Trinitrophloroglucinol (2,4,6-Trinitrobenzene-1,3,5-triol)
[4328-17-0] **$C_6H_3N_3O_9$**

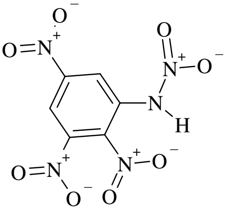


1. Sorbe, 1968, 153
2. DeFusco, A. A., *Org. Prep. Proced. Int.*, 1982, **14**, 393—395

It explodes on heating [1], and an improved preparation is described [2]. The compound has +20% oxygen balance, so can function as an overall oxidant. It would also be expected to form explosive metal salts.

See other POLYNITROARYL COMPOUNDS

2114. *N*,2,3,5-Tetranitroaniline
[57204-58-7] **$C_6H_3N_5O_8$**



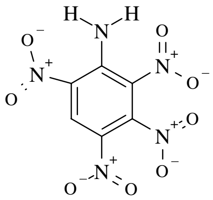
1. Mudge, P. R. *et al., J. Chem. Soc., Chem. Comm.*, 1975, 569
2. Meldola, R. *et al., J. Chem. Soc.*, 1905, **87**, 1204, 1205

Thermal rearrangement to the internal salt, 3,5-dinitrobenzenediazonium 2-oxide, and nitric acid proceeds explosively in absence of solvent [1]. The oxide itself explodes violently at 190°C [2].

See other N—NITRO COMPOUNDS, POLYNITROARYL COMPOUNDS

2115. 2,3,4,6-Tetranitroaniline

[3698-54-2] **$C_6H_3N_5O_8$**



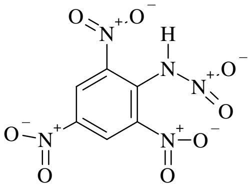
Preparative hazard

See 3-Nitroaniline: Nitric acid, Sulfuric acid

See other POLYNITROARYL COMPOUNDS

2116. *N*,2,4,6-Tetranitroaniline

[4591-46-2] **$C_6H_3N_5O_8$**



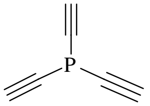
Olsen, R. E. *et al., ACS 54*, 1966, 50

Impure tetryl must be recrystallised with care as it may deflagrate at only 50°C.

See other N—NITRO COMPOUNDS, POLYNITROARYL COMPOUNDS

2117. Triethynylphosphine

[687-80-9] **C_6H_3P**



Voskuil, W. *et al., Rec. Trav. Chim.*, 1964, **83**, 1301

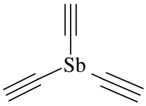
It explodes on strong friction, and on standing it decomposes and may then explode spontaneously.

See other ACETYLENIC COMPOUNDS

See related ALKYLPHOSPHINES

2118. Triethynylantimony

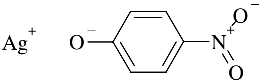
[687-81-0] **C_6H_3Sb**



Voskuil, W. *et al., Rec. Trav. Chim.*, 1964, **83**, 1301
It explodes on strong friction.
See other METAL ACETYLIDES

2119. Silver 4-nitrophenoxide

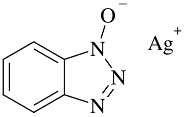
[86255-25-6] **$C_6H_4AgNO_3$**



Spiegel, L. *et al., Ber.*, 1906, **39**, 2639
A sample decomposed explosively after intensive drying at 110°C. The *aci*-nitro-*p*-quinonoid salt may have been formed.
See other METAL NITROPHENOXIDES, SILVER COMPOUNDS
See related aci-NITROQUINONOID COMPOUNDS

2120. Silver benzo-1,2,3-triazole-1-oxide

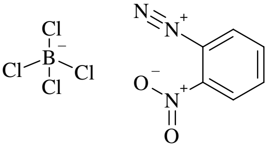
[93693-72-2] **$C_6H_4AgN_3O$**



Deorha, D. S. *et al., J. Indian Chem. Soc.*, 1964, **41**, 793
It is unsuitable as a gravimetric precipitate, as it explodes on heating rather than smoothly giving weighable silver.
See other N—O COMPOUNDS, SILVER COMPOUNDS, TRIAZOLES

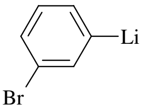
2121. 2-Nitrobenzenediazonium tetrachloroborate

[ ] **$C_6H_4BCl_4N_3O_2$**



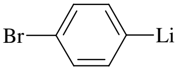
See entry DIAZONIUM TETRAHALOBORATES

2122. 3-Bromophenyllithium
[2592-86-1] **C_6H_4BrLi**



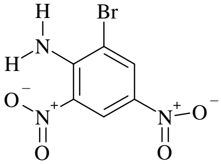
See entry ORGANOLITHIUM REAGENTS
See other HALO-ARYLMETALS

2123. 4-Bromophenyllithium
[22480-64-4] **C_6H_4BrLi**



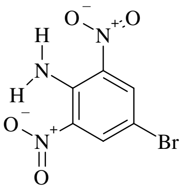
Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 65
It explodes if traces of oxygen are present in the inert atmosphere needed for the preparation.
See entry ORGANOLITHIUM REAGENTS
See other HALO-ARYLMETALS

2125. 2-Bromo-4,6-dinitroaniline
[1817-73-8] **$C_6H_4BrN_3O_4$**



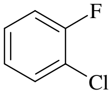
This and the 4-bromo-2,6-dinitro analogue show local decomposition on moderate heating.
See entry HIGH RATE DECOMPOSITION

2126. 4-Bromo-2,6-dinitroaniline
[62554-90-9] **$C_6H_4BrN_3O_4$**



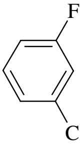
This and the 2-bromo-4,6-dinitro analogue show local decomposition on moderate heating.
See entry HIGH RATE DECOMPOSITION

†2127. 2-Chlorofluorobenzene
[348-51-6] **C_6H_4ClF**



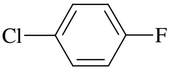
See other HALOARYL COMPOUNDS

†2128. 3-Chlorofluorobenzene
[625-98-9] **C_6H_4ClF**



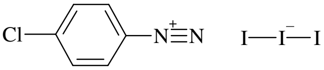
See other HALOARYL COMPOUNDS

†2129. 4-Chlorofluorobenzene
[352-33-0] **C_6H_4ClF**



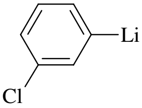
See other HALOARYL COMPOUNDS

2130. 4-Chlorobenzenediazonium triiodide
[68596-93-0] **$C_6H_4ClI_3N_2$**



See entry DIAZONIUM TRIIODIDES

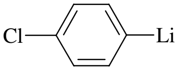
2131. 3-Chlorophenyllithium
[25077-87-6] **C_6H_4ClLi**



See entry ORGANOLITHIUM REAGENTS
See other HALO-ARYLMETALS

2132. 4-Chlorophenyllithium

[14774-78-8] **C_6H_4ClLi**



Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 65

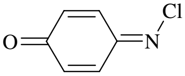
It explodes if traces of oxygen are present in the inert atmosphere needed for the preparation.

See entry ORGANOLITHIUM REAGENTS

See other HALO-ARYLMETALS

2133. 1,4-Benzoquinone-4-chloroimine

[637-61-6] **C_6H_4ClNO**



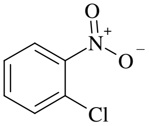
Sorbe, 1968, 112

It explodes on heating, like the bis-chloroimine.

See other N-HALOGEN COMPOUNDS

2134. 2-Chloronitrobenzene

[88-73-3] **$C_6H_4ClNO_2$**



Energy of decomposition (in range 350—450°C) measured as 1.83 kJ/g by DSC, and T_{ait24} was determined as 264°C by adiabatic Dewar tests, with an apparent energy of activation of 173 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkalis, Alcohols

See 4-Nitrochlorobenzene, next below

Ammonia

1. *MCA Case History No. 1624*
2. Vincent, G. C., *Loss. Prev.*, 1971, **5**, 46—52
3. Jacobson, O. F., *Proc. 3rd Int. Sympos. Loss Prev. Safety Prom. Proc. Ind.*, 417—421, SSCI, Basle, 1982
4. Gordon, M. D. *et al., Plant/Oper. Progr.*, 1982, **1**, 27—33

During the large-scale preparation of 2-nitroaniline at 160—180°C/30—40 bar in a jacketed autoclave, several concurrent processing abnormalities (excess chloro compound, too little ammonia solution, failure to apply cooling or to vent the autoclave and non-failure of a rupture-disk) led to a runaway reaction and pressure-explosion of the vessel [1]. A full analysis of the incident is published [2]. A retrospective hazard and operability study revealed that 6 simultaneous fault conditions had been involved [3], and the thermal stability of the amination process for manufacturing 2-nitroaniline was studied using mathematical modelling techniques [4]. The results of modelling the process abnormalities closely followed the actual events [1,2].

See other AMINATION INCIDENTS

2-Ethylhexylamine

1. U. S. Chemical Safety and Hazard Investigation Board, 2000, Report No. 1998-06-1-NJ
2. Joseph, G. *et al., Proc. 36th Ann. Loss. Prevent. Symp.*, 2002, 494, AIchE
3. Editor's comments, 2002

A fuel colorant was manufactured by heating together this amine and chloronitrobenzene. The exothermic reaction starts just above room temperature but was operated at 150°C [this is probably because salt formation drastically reduces amine availability in the latter half of the reaction - Ed.]. The product decomposes, by a presumably still more exothermic reaction, from 195°C. The process was operated as a batch reaction (all reagents charged at the start) in a 2000 gal (8000 l) vessel under manual control: an initial burst of heating, followed by cooling to remove reaction heat. Control was lost, and the hatch blown off the vessel, the escaped contents producing a fire and nine walking wounded. There had been vessel changes which probably reduced the cooling capacity [1, 2]. Not considered in the Report is the implication of a process operated for more than eight years, but of which this was only the thirtyfirst batch. Very short campaigns, operated at very long intervals, do not allow operators to become familiar with a process. None the less, managers will commonly be convinced that a long established process is well understood and requires no special care and supervision [3]. As is usual over such time periods, a significant part (product instability) of what understanding there had once been in management had also been lost.

Methanol , Sodium hydroxide

1. Klais, O. *et al., Prax. Sicherheitstech.*, 1997, **4**, 41
2. Klais, O *et al.*, in *Safety and Runaway Reactions*, Smeder, B & Mitchison, N. (Eds.), EUR 17723 EN, European Commission, 1997

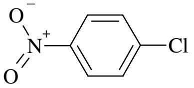
A very large scale reaction to produce 2-nitroanisole from chloronitrobenzene and methanolic sodium hydroxide ran out of control and painted the town orange. This was attributed to reduction of the nitro group at temperatures above 100°C, a far more exothermic reaction than intended. This temperature was reached because the methanolic alkali was charged without agitation, and, the reaction not starting, the batch was heated to 90°C. The agitation was only then switched on.

See also 4-Nitrochlorobenzene, next below

See other AGITATION INCIDENTS, HALOARYL COMPOUNDS, NITROARYL COMPOUNDS

2135. 4-Chloronitrobenzene

[100-00-5] **$C_6H_4ClNO_2$**



HCS 1980, 308

1. Doyle, W. H., *Loss. Prev.*, 1969, **3**, 16

A steam-heated still used to top the crude material exploded

Energy of decomposition (in range 300—450°C) measured as 2.05 kJ/g by DSC, and T_{ait24} was determined as 275°C by adiabatic Dewar tests, with an apparent energy of activation of 172 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkalis, Alcohols

1. Anderson, H. L. *et al., Thermochim. Acta*, 1996, 271, 195
2. Anderson, H. L. *et al., Loss Prevention and Safety Promotion in the Process Industries*, Vol II, (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 387, Amsterdam, Elsevier, 1995

A calorimetric study of reaction with sodium or potassium hydroxides in ethanol or 2-propanol is given. At starting temperatures below 70°C the product is the appropriate nitrophenyl ether; above that temperature, reduction of the nitro groups may come into play, to give much more energy and a variety of other products. This reaction is inhibited by oxygen. There is potential for runaway if such reactions are operated industrially with poor temperature control. The editor suspects that the stimulus for this study was an accident which sprayed the German environment with 2-nitroanisole.

See Sodium methoxide; below

Potassium hydroxide

Mixtures with potassium hydroxide (1:1.5 mol) deflagrate readily at a rate of 1.3 cm/min.

See entry NITROAROMATIC—ALKALI HAZARDS, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 3)

See other DEFLAGRATION INCIDENTS

Sodium methoxide

Anon., *ABCM Quart. Safety Summ.*, 1944, **15**, 15

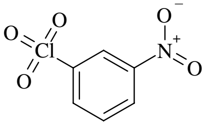
Addition of the chloro compound to a solution of sodium methoxide in methanol caused an unusually exothermic reaction to occur. The lid of the 450 l vessel was blown off, and a fire and explosion followed. No cause for the unusual vigour of the reaction was found.

See Alkalis, Alcohols; above

See other HALOARYL COMPOUNDS, NITROARYL COMPOUNDS

2136. 3-Nitroperchlorylbenzene

[20731-44-6] **$C_6H_4ClNO_5$**



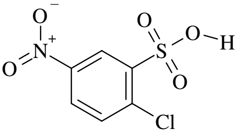
McCoy, G., *Chem. Eng. News*, 1960, **38**(4), 62

The nitration product of perchloryl benzene is explosive, comparable in shock-sensitivity with lead azide, with a very high propagation rate.

See other NITROARYL COMPOUNDS, PERCHLORYL COMPOUNDS

2137. 2-Chloro-5-nitrobenzenesulfonic acid

[96-73-1] **$C_6H_4ClNO_5S$**



Preparative hazard

Exothermic decomposition of the acid at 150°C (Q = 0.708 kJ/g) is time-delayed, may be faster in a closed than an open system, and is dangerous.

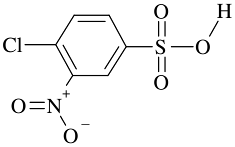
See Sulfuric acid: 4-Chloronitrobenzene

See entry SELF-ACCELERATING REACTIONS

See other HALOARYL COMPOUNDS, NITROARYL COMPOUNDS, ORGANIC ACIDS

2138. 4-Chloro-3-nitrobenzenesulfonic acid

[71799-32-1] **$C_6H_4ClNO_5S$**



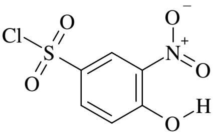
Négyesi, G., *Process Safety Progress*, 1996, **15**(1), 42

This compound shows signs of impact and friction sensitivity.

See other NITROARYL COMPOUNDS

2139. 4-Hydroxy-3-nitrobenzenesulfonyl chloride

[147682-51-7] **$C_6H_4ClNO_5S$**



Vervalin, C. H., *Hydrocarbon Proc.*, 1976, **55**(9), 321—322

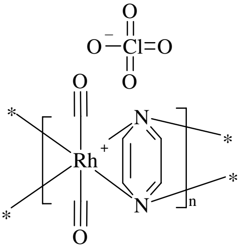
The chloride, produced by interaction of 2-nitrophenol and chlorosulfuric acid at 4°C, decomposed violently during discharge operations from the 2000 l vessel, leaving a glowing residue. It was subsequently found that accelerating exothermic decomposition sets in at 24—27°C.

See other NITROACYL HALIDES

See related SULFONATION INCIDENTS

2140. Dicarbonylpyrazinerhodium(I) perchlorate

[ ] **$C_6H_4ClN_2O_6Rh$**



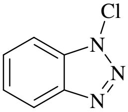
Uson, R. *et al., J. Organomet. Chem.*, 1981, **220**, 109

This (notably) and other polynuclear complexes exploded violently on heating during microanalysis.

See related AMMINEMETAL OXOSALTS

2143. 1-Chlorobenzotriazole

[21050-95-3] **$C_6H_4ClN_3$**



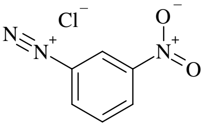
Hopps, H. B., *Chem. Eng. News*, 1971, **49**(30), 3

Spontaneous ignition occurred during packing operations.

See other N-HALOGEN COMPOUNDS

2144. 3-Nitrobenzenediazonium chloride

[2028-76-4] **$C_6H_4ClN_3O_2$**



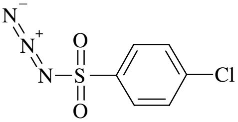
Potassium *O*-ethyldithiocarbamate

See DIAZONIUM SULFIDES AND DERIVATIVES

See other DIAZONIUM SALTS

2145. 4-Chlorobenzenesulfonyl azide

[4547-68-6] **$C_6H_4ClN_3O_2S$**



N-Methyltetrahydro-β-carboline

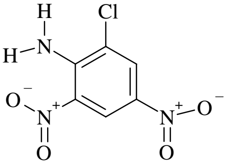
Bailey, A. S. *et al., J. Chem. Soc., Perkin Trans. 1*, 1980, 1513

In absence of solvent chloroform, interaction at ambient temperature is explosive.

See other ACYL AZIDES

2146. 2-Chloro-4,6-dinitroaniline

[3531-19-9] **$C_6H_4ClN_3O_4$**



The solid amine can be caused to detonate by heating, or by a powerful initiating charge, and fast local decomposition occurs on heating moderately.

See entry HIGH RATE DECOMPOSITION

Nitrosylsulfuric acid

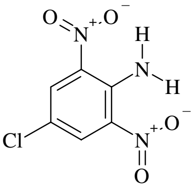
Bersier, P. *et al., Chem. Ing. Tech.*, 1971, **43**, 1311—1315

Diazotisation of the potentially explosive 2-chloro-4,6-dinitroaniline in the third batch of a new process (at a higher than usual concentration in 40% nitrosylsulfuric acid) led to a violent explosion soon after the temperature had been increased to 50°C. Subsequent DSC work showed that the temperature at which thermal decomposition of the diazonium sulfate solution or suspension sets in is inversely proportional to the concentration of amine, falling from 160°C at 0.3 mmol/g to 80°C at 2 mmol/g. Thermal stability of 17 other diazonium derivatives was similarly investigated.

See other DIAZONIUM SULFATES, POLYNITROARYL COMPOUNDS

2147. 4-Chloro-2,6-dinitroaniline

[5388-62-5] **$C_6H_4ClN_3O_4$**

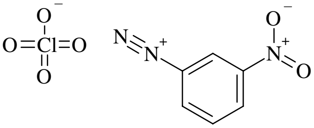


CHETAH, 1990, 183
Can be caused to detonate by 50 g tetryl booster.

Nitrosylsulfuric acid
Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 62
During large-scale diazotisation of the amine, severe local overheating is thought to have caused the explosion observed. The effect could not be reproduced in the laboratory.
See DIAZOTISATION
See other POLYNITROARYL COMPOUNDS

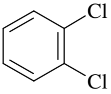
Preparative hazard
See Nitric acid: 4-Chloro-2-nitroaniline

2148. 3-Nitrobenzenediazonium perchlorate
[22751-24-2] **$C_6H_4ClN_3O_6$**



Schumacher, 1960, 205
Explosive, very sensitive to heat or shock.
See other DIAZONIUM PERCHLORATES

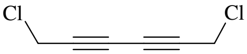
2149. 1,2-Dichlorobenzene
[95-50-1] **$C_6H_4Cl_2$**



Aluminium, Halocarbons
See Aluminium: Halocarbons (reference 5)

Other reactants
Yoshida, 1980, 156
MRH values calculated for 13 combinations with oxidants are given.
See other HALOARYL COMPOUNDS

2150. 1,6-Dichloro-2,4-hexadiyne
[16260-59-6] **$C_6H_4Cl_2$**



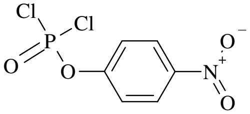
1. Driedger, P. E. *et al., Chem. Eng. News*, 1972, **50**(12), 51
2. Whiting, M. C., *Chem. Eng. News*, 1972, **50**(23), 86
3. Ford, M *et al., Chem. Eng. News*, 1972, **50**(30), 67
4. Walton, D. R. M., private comm., 1987
5. Anon., *Inst. Univ. Saf. Officers Bull.*, 1987, (8), 9

It is extremely shock-sensitive, a 4.0 kgcm shock causing detonation in 50% of test runs (cf. 3.5 kgcm for propargyl bromide; 2.0 kgcm for glyceryl nitrate). The intermediate bis-chlorosulfite involved in the preparation needs low temperatures to avoid vigorous decomposition. The corresponding diiodo derivative was expected to be similarly hazardous [1], and this has been confirmed [2]. Improvements in preparative techniques (use of dichloromethane solvent at —30°C) to avoid violent reaction have also been described [3]. An attempt to distill the compound (b.p. 55—58°C/0.6 mbar, equivalent to about 230°C/1 bar) at atmospheric pressure from a heating mantle led to a violent explosion [4]. The compound involved was erroneously given as 1,6-dichloro-2,4-hexadiene [5].

See other HALOACETYLENE DERIVATIVES

2151. 4-Nitrophenylphosphorodichloridate

[777-52-6] **$C_6H_4Cl_2O_4P$**



Frommer, M. A. *et al.*, 1990, US Pat. 4910190; *Chem. Abs.*, 1991, **114**, 122705b

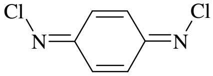
This compound may decompose violently during distillation.

See other NITROARYL COMPOUNDS

See related NON-METAL HALIDES (AND THEIR OXIDES)

2152. Benzoquinone 1,4-bis(chloroimine) (1,4-Bis(chlorimido)-2,5-cyclohexadiene)

[637-70-7] **$C_6H_4Cl_2N_2$**



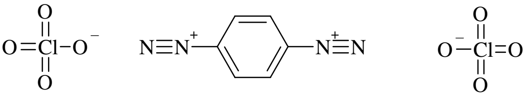
Sorbe, 1968, 112

It explodes on heating, like the mono-chloroimine.

See other N-HALOGEN COMPOUNDS

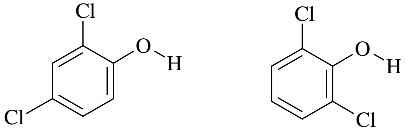
2153. Benzene-1,4-bis(diazonium perchlorate)

[43008-25-9] **$C_6H_4Cl_2N_4O_8$**



Hofman, K.A. *et al., Ber.,* 1910 **43**, 2624
Described by Hofman as the most powerfully explosive compound of which he knew. Since it is of better oxygen balance than the aromatic high explosives, and the diazonium unit is also high energy, this is quite probable.
See DIAZONIUM PERCHLORATES

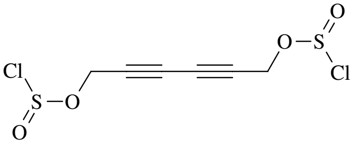
2154. Dichlorophenol mixed isomers
[25167-81-1] **$C_6H_4Cl_2O$**



HCS 1980, 381 (2,4-Dichlorophenol)

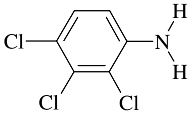
Laboratory Chemical Disposal Co. Ltd., confidential information, 1968
During vacuum fractionation of the mixed dichlorophenols produced by partial hydrolysis of trichlorobenzene, rapid admission of air to the receiver caused the column contents to be forced down into the boiler at 210°C, and a violent explosion ensued.
See other HALOARYL COMPOUNDS

2155. 2,4-Hexadiynylene chlorosulfite
[73506-30-6] **$C_6H_4Cl_2O_4S_2$**



Driedger, P. E. *et al., Chem. Eng. News*, 1972, **50**(12), 51
This is probably an intermediate in the preparation of the 1,6-dichloro compound from 2,4-hexadiyne-1,6-diol and thionyl chloride in DMF. The reaction mixture must be kept at a low temperature to avoid vigorous decomposition and charring. This may be due to interaction with the solvent.
See 2,4-Hexadiynylene chloroformate
See also Dimethylformamide
See other ACETYLENIC COMPOUNDS, ACYL HALIDES

2156. 2,3,4-Trichloroaniline
[634-67-3] **$C_6H_4Cl_3N$**

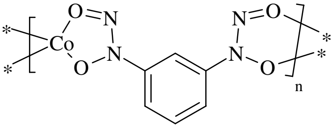


Energy of decomposition (in range 220—400°C) measured as 0.21 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other HALOANILINES

2157. Cobalt(II) chelate of 1,3-bis(*N*-nitrosohydroxylamino)benzene

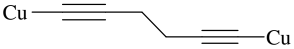
[27662-11-9] **$C_6H_4CoN_4O_4$**



Battei, R. S. *et al., J. Inorg. Nucl. Chem.*, 1970, **32**, 1525
The cobalt(II) chelate of 'dicupferron' explodes on heating at 205°C.
See Cobalt(II) chelate of bi(1-hydroxy-3,5-diphenylpyrazol-4-yl *N*-oxide)
See other N—O COMPOUNDS

2158. Dicopper(I) 1,5-hexadiynide

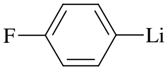
[86425-12-9] **$C_6H_4Cu_2$**



Chow, Y. L. *et al., Can. J. Chem.*, 1983, **61**, 795—800
It exploded when dried in a desiccator.
See other METAL ACETYLIDES

2159. 4-Fluorophenyllithium

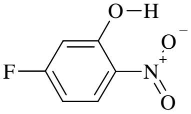
[1493-23-8] **C_6H_4FLi**



See entry ORGANOLITHIUM REAGENTS
See other HALO-ARYLMETALS

2160. 5-Fluoro-2-nitrophenol

[446-36-6] **$C_6H_4FNO_3$**



Preparative hazard

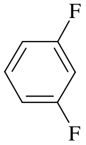
Robinson, N., *Chem. Brit.*, 1987, **23**, 837
Following a patented procedure for the conversion of 2,4-dinitrochlorobenzene to 5-chloro-2-nitrophenol, 2,4-difluoronitrobenzene was treated with sodium hydroxide in

hot aqueous dioxane containing a phase transfer catalyst. On the small scale, the reaction and isolation of 5-fluoro-2-nitrophenol, including vacuum distillation, were uneventful. On the 20 l scale, vacuum distillation of combined batches of the crude product led to onset of decomposition at 150°C, which could not be controlled, and the residue erupted with explosive violence and a small fire ensued. Thermal examination of fresh small-scale crude material has shown that it is capable of highly exothermic decomposition, with onset of the exotherm at 150°C (ARC). It was then realised that difficulty in controlling the reaction temperature had been experienced on the 20 l scale. It is recommended that this procedure and purification should not be attempted on so large a scale.

See other NITROARYL COMPOUNDS

†2161. 1,3-Difluorobenzene

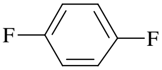
[372-18-9] **$C_6H_4F_2$**



See other HALOARYL COMPOUNDS

†2162. 1,4-Difluorobenzene

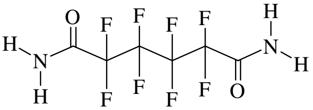
[540-36-3] **$C_6H_4F_2$**



See other HALOARYL COMPOUNDS

2163. Octafluoroadipamide

[355-66-8] **$C_6H_4F_8N_2O_2$**

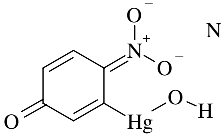


Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Fluoroamides

2164. Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide

[ ] **$C_6H_4HgNNaO_4$**



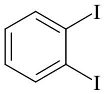
Hantzsch, A. *et al., Ber.*, 1906, **39**, 1115

This salt of the *aci-p*-quinonoid form of 2-hydroxymercurio-4-nitrophenol explodes on heating.

See other aci-NITROQUINONOID COMPOUNDS, MERCURY COMPOUNDS

2165. 1,2-Diiodobenzene

[615-42-9] **$C_6H_4I_2$**



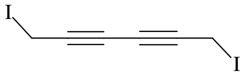
Rüst, 1948, 302

A small sample in a sealed glass capillary exploded violently at 181°C, breaking the surrounding oil bath.

See other HALOARYL COMPOUNDS, IODINE COMPOUNDS

2166. 1,6-Diiodo-2,4-hexadiyne

[44750-17-6] **$C_6H_4I_2$**

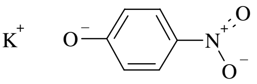


See 1,6-Dichloro-2,4-hexadiyne

See other HALOACETYLENE DERIVATIVES

2167. Potassium 4-nitrophenoxide

[1124-31-8] **$C_6H_4KNO_3$**



1. L. Bretherick, Personal experience
2. Thorpe's Dictionary of Applied Chemistry; 4th Edn., London, 1940, **IV**, 475

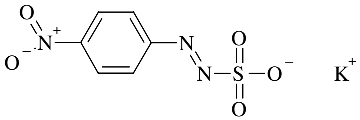
A sample of this potassium salt exploded after long storage in a non-evacuated desiccator [1]. This may have been caused by formation of some tautomeric *aci*-quinonoid salt (IIa) by prolonged desiccation. This compound had earlier been described as exploding on percussion [2].

See 4-Nitrophenol: Potassium hydroxide

See other aci-NITROQUINONOID COMPOUNDS, METAL NITROPHENOXIDES, NITROARYL COMPOUNDS

2168. Potassium 4-nitrobenzeneazosulfonate

[ ] **$C_6H_4KN_3O_5S$**



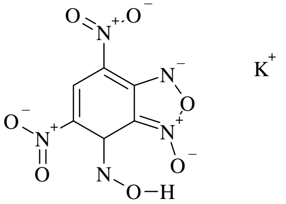
491M, 1975, 345

During examination of a 10 g batch of the crystalline material on a filter paper using a hand lens, it exploded. This was attributed to sudden rearrangement of the metastable syn- to the anti-form (perhaps triggered by light energy concentrated by the lens).

See other AZO COMPOUNDS, N—S COMPOUNDS

2169. Potassium 4-hydroxyamino-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide

[86341-95-9] **$C_6H_4KN_5O_7$**



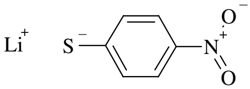
Norris, W. P. *et al., Chem. Abs.*, 1983, **99**, 40662

Sensitivity to mechanical, electrostatic and thermal shock is typical of a primary explosive.

See other FURAZAN N-OXIDES

2170. Lithium 4-nitrothiophenoxide

[78350-94-4] **$C_6H_4LiNO_2S$**



1. Julia, M., *Chem. & Ind.*, 1981, 130; *Chem. Eng. News*, 1981, **59**(14), 3
2. Bretherick, L., *Chem. & Ind.*, 1981, 202; *Chem. Eng. News*, 1981, **59**(31), 3

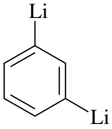
A vacuum dried sample of the salt exploded violently when exposed to air [1]. It was postulated that the *aci*-quinonoid species may have been the unstable species [2].

See other aci-NITROQUINONOID COMPOUNDS, NITROAROMATIC—ALKALI HAZARDS

See related METAL NITROPHENOXIDES

2171. 1,3-Dilithiobenzene

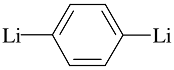
[2592-85-0] **$C_6H_4Li_2$**



See entry ORGANOLITHIUM REAGENTS
See other ARYLMETALS

2172. 1,4-Dilithiobenzene

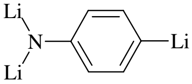
[7270-42-0] **$C_6H_4Li_2$**



See entry ORGANOLITHIUM REAGENTS
See other ARYLMETALS

2173. *N,N*,4-Trilithioaniline

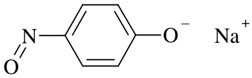
[ ] **$C_6H_4Li_3N$**



Gilman, H. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 2934
Highly explosive in contact with air.
See other N-METAL DERIVATIVES, ORGANOMETALLICS

2174. Sodium 4-nitrosophenoxide

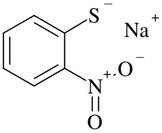
[823-87-0] **$C_6H_4NNaO_2$**



Sorbe, 1968, 86
The dry solid tends to ignite.
See other NITROSO COMPOUNDS

2175. Sodium 2-nitrothiophenoxide

[22755-25-5] **$C_6H_4NNaO_2S$**



Davies, H. J., *Chem. & Ind.*, 1966, 257

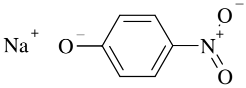
The material exploded when the temperature of evaporation of the slurry was increased by adding a higher-boiling solvent. This may have been caused by presence of some of the tautomeric *aci*-nitro-*o*-thioquinone. Such salts are thermally unstable.

See other aci-NITROQUINONOID COMPOUNDS, NITROAROMATIC—ALKALI HAZARDS

See related METAL NITROPHENOXIDES

2176. Sodium 4-nitrophenoxide

[824-78-2]] **$C_6H_4NNaO_3$**



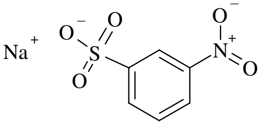
1. Semiganowski, N., *Z. Anal. Chem.*, 1927, **72**, 29
2. Baltzer, private comm., 1976

An ammoniacal solution of 4-nitroaniline containing ammonium chloride was being treated with 50% sodium hydroxide solution to displace ammonia. In error, double the amount required to give the usual 10% of free alkali was added, and during the subsequent degassing operation (heating to 130°C under pressure, followed by depressuring to vent ammonia), complete conversion to sodium 4-nitrophenoxide occurred unwittingly [1]. This solid product, separated by centrifuging, was then heated to dry it, when it decomposed violently and was ejected through the vessel opening like a rocket [2]. Some of the tautomeric *aci*-nitroquinonoid salt may have been produced during the drying operation.

See other aci-NITROQUINONOID COMPOUNDS, METAL NITROPHENOXIDES, NITROAROMATIC—ALKALI HAZARDS

2177. Sodium 3-nitrobenzenesulfonate

[127-68-4] **$C_6H_4NNaO_5S$**



1. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

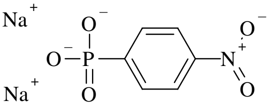
It ignites at 335°C and the deflagration rate of the solid is 4.5 cm/min [1]. T_{ait24} was determined as 305°C by adiabatic Dewar tests, with an apparent energy of activation of 441 kJ/mol [2].

See 3-Nitrobenzenesulfonic acid

See other DEFLAGRATION INCIDENTS, NITROARYL COMPOUNDS

2178. Disodium 4-nitrophenylphosphate

[4264-83-9] **$C_6H_4NNa_2O_6P$**



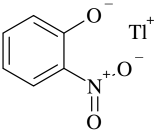
Preparative hazard

See Nitric acid: Disodium phenyl orthophosphate

See other NITROARYL COMPOUNDS

2179. Thallium(I) 2-nitrophenoxide

[32707-02-1] **$C_6H_4NO_3Tl$**



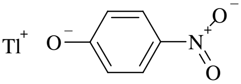
Langhans, A., *Z. Ges. Schiess.- Sprengstoff W.*, 1936, **31**, 359, 361

Explodes on heating.

See other HEAVY METAL DERIVATIVES, METAL NITROPHENOXIDES, NITROARYL COMPOUNDS

2180. Thallium(I) 4-nitrophenoxide

[32707-03-2] **$C_6H_4NO_3Tl$**



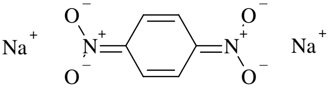
Langhans, A., *Z. Ges. Schiess.- Sprengstoff W.*, 1936, **31**, 359, 361

Explodes on heating.

See other HEAVY METAL DERIVATIVES, METAL NITROPHENOXIDES, NITROARYL COMPOUNDS

2181. Sodium 1,4-bis(*aci*-nitro)-2,5-cyclohexadienide ([μ-(1,4-Dinitrocyclohexa-2,5-dienediyl)]disodium)

[89592-54-1] **$C_6H_4N_2Na_2O_4$**

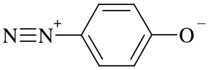


Meisenheimer, J. *et al., Ber.*, 1906, **39**, 2529

The sodium and potassium salts of the bis-*aci*-quinonoid form of 1,4-dinitrobenzene deflagrate on heating.

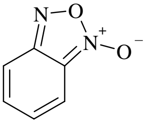
See other aci-NITROQUINONOID COMPOUNDS

2182. Benzenediazonium-4-oxide
[6925-01-5] **$C_6H_4N_2O$**



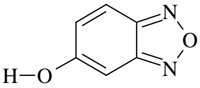
Hantzsch, A. *et al., Ber.*, 1896, **29**, 1530
It decomposes violently at 75°C.
See other ARENEDIAZONIUM OXIDES

2183a. Benzofurazan-*N*-oxide
[480-96-6] **$C_6H_4N_2O_2$**



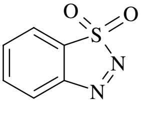
CHETAH, 1990, 188
Shock sensitive (probably not very).
See other FURAZAN N-OXIDES

2183b. 5-Hydroxybenzofurazan (5-Benzofurazanol)
[768-09-2] **$C_6H_4N_2O_2$**



Ruggeri, S. G. *et al., Org. Process Res. & Dev.*, 2003, **7**(6), 1043
The compound was judged too unstable, and too energetic, to risk using it in industrial scale pharmaceutical synthesis.

2184. Benzo-1,2,3-thiadiazole 1,1-dioxide
[37150-27-9] **$C_6H_4N_2O_2S$**

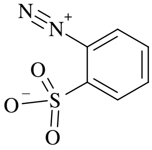


1. Wittig, G. *et al., Chem. Ber.*, 1962, **95**, 2718
2. Wittig, G. *et al., Org. Synth.*, 1967, **47**, 6

The solid explodes at 60°C, on impact or friction, or sometimes spontaneously. Solutions decompose below 10°C to give benzyne [1]. Full preparative and handling details are given [2].
See other N—S COMPOUNDS

2185. Benzenediazonium-2-sulfonate

[612-31-7] **$C_6H_4N_2O_3S$**



Franklin, E. C., *Amer. Chem. J.*, 1899, **20**, 459

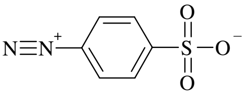
The internal diazonium salt explodes on contact with flame or on percussion.

See other DIAZONIUM SALTS

See related DIAZONIUM CARBOXYLATES

2186. Benzenediazonium-4-sulfonate

[305-80-6] **$C_6H_4N_2O_3S$**



1. Wichelhaus, H., *Ber.*, 1901, **34**, 11
2. Anon., *Sichere Chemiearb.*, 1959, **11**, 59
3. Anon., *Sichere Chemiearb.*, 1978, **30**, 77

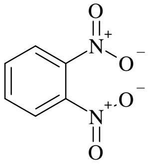
This internal salt of diazotised sulfanilic acid (Pauly's reagent) exploded violently on touching when thoroughly dry [1]. Use of a metal spatula to remove a portion of a refrigerated sample of the solid salt caused a violent explosion [2], and a similar incident was reported 19 years later [3]. All solid diazo compounds must be stored only in small quantity under refrigeration in loosely plugged containers. Handle gently with non-metallic spatulae using personal protection [2].

See other DIAZONIUM SALTS

See related DIAZONIUM CARBOXYLATES

2187. 1,2-Dinitrobenzene

[528-29-0] **$C_6H_4N_2O_4$**



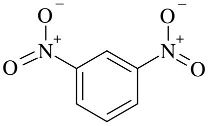
Nitric acid

See Nitric acid: Nitroaromatics

See other POLYNITROARYL COMPOUNDS

2188. 1,3-Dinitrobenzene

[99-65-0] **$C_6H_4N_2O_4$**



Anon., *Sichere Chemiearbeit*, 1993, **45**(7), 82

Heat of decomposition was determined as 4.6 kJ/g (c.f. MRH calculated value of 5.02). T_{ait24} was determined as 284°C by adiabatic Dewar tests, with an apparent energy of activation of 284 kJ/mol.

A vessel containing dinitrobenzene for drying, after washing out styphnic and picric acid byproducts in alkali, retained a heel of some hundreds of litres, with a residue of rust, after emptying. This was cleaned out with low pressure steam at 130°C every two years. During cleaning, the tank burst and burnt out. It was supposed that residual nitrophenol salts had accumulated on the rust, which was shown to thermally sensitise them, and deflagrated, initiating the dinitrobenzene.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (references 1, 2)

Nitric acid

See Nitric acid: Nitroaromatics

Other reactants

Yoshida, 1980, 160

MRH values calculated for 7 combinations with materials catalysing its decomposition are given.

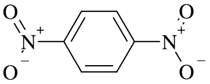
Tetranitromethane

See Tetranitromethane: Aromatic nitro compounds

See other POLYNITROARYL COMPOUNDS

2189. 1,4-Dinitrobenzene

[100-25-4] **$C_6H_4N_2O_4$**



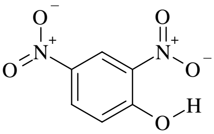
Nitric acid

See Nitric acid: Nitroaromatics

See other POLYNITROARYL COMPOUNDS

2190. 2,4-Dinitrophenol

[51-28-5] **$C_6H_4N_2O_5$**



NSC 690, 1981; *HCS 1980*, 439

T_{ait24} was determined as 189°C by adiabatic Dewar tests, with an apparent energy of activation of 144 kJ/mol. Dinitrophenol is now classified as an explosive in the UK, and is normally available from laboratory suppliers wetted with 15% water, as is picric acid. *See entry* THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2).

Bases

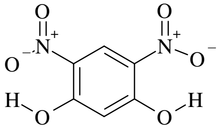
1. Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389—390
2. *Thorpe's Dictionary of Applied Chemistry*; London, 1940, **IV**, 477

Dinitrophenol forms explosive (*aci*-quinonoid ?) salts with alkalies or ammonia, and should not be heated with them in closed vessels [1]. Dinitrophenol forms explosive salts with most metals [2].

See Sodium 2,4-dinitrophenoxide

See other aci-NITROQUINONOID COMPOUNDS, NITROAROMATIC—ALKALI HAZARDS, POLYNITROARYL COMPOUNDS

2191. 4,6-Dinitro-1,3-benzenediol (4,6-Dinitroresorcinol)
[616-74-0] **$C_6H_4N_2O_6$**



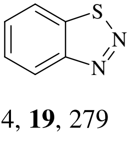
Preparative hazard

Schmitt., R. J. *et al., J. Org. Chem.*, 1988, **53**, 5568—5569

The reaction conditions necessary to obtain a good yield of the title compound (a difficult isomer), and to avoid hazards during the nitration of resorcinol , are critical and strict adherence to those specified is essential. The necessary 80% white fuming nitric acid must be completely free from oxides of nitrogen and nitrous acid, and procedures for this are detailed. Then the temperature during addition of the diacetate must be kept between —10 and 0°C by regulating the rate of addition. The alternative use of 80% sulfuric acid as solvent for the 80% nitric acid (5 equiv.) is preferred as more reliable, but both methods have led to violent exothermic decomposition, accompanied by fume-off, after an induction period. In any event, the explosive 2,4,6-trinitroresorcinol ('styphnic acid') is produced as a by-product.

See other INDUCTION PERIOD INCIDENTS, NITRATION INCIDENTS, POLYNITROARYL COMPOUNDS

2192. Benzo-1,2,3-thiadiazole
[273-77-8] **$C_6H_4N_2S$**



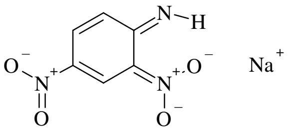
Jordis, U. *et al., Phos. Sulfur*, 1984, **19**, 279

Purification by extraction and then distillation led to violent decomposition. Steam distillation avoided this problem.

See other N—S COMPOUNDS

2193. Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide

[ ] **$C_6H_4N_3NaO_4$**



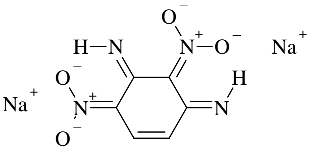
Green, A. G. *et al., J. Chem. Soc.*, 1913, **103**, 508—513

The sodium and potassium salts of the mono-*aci-o*-quinonoid form of 2,4-dinitroaniline readily deflagrate on heating.

See other aci-NITROQUINONOID COMPOUNDS, POLYNITROARYL COMPOUNDS

2196. Sodium 3,5-bis(*aci*-nitro)cyclohexene-4,6-diiminide

[ ] **$C_6H_4N_4Na_2O_4$**



Alone, or Water

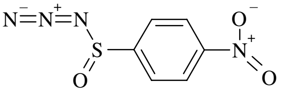
Meisenheimer, J. *et al., Ber.*, 1906, **39**, 2538

The disodium salt of the bis-*aci-o*-quinonoid form of 2,4-dinitro-1,3-phenylenediamine deflagrates violently in contact with heat or moisture.

See other aci-NITROQUINONOID COMPOUNDS

2197. 4-Nitrobenzenesulfinyl azide

[53852-44-1] **$C_6H_4N_4O_3S$**

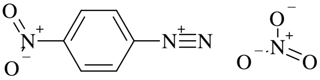


See entry SULFINYL AZIDES

See other ACYL AZIDES

2198. 4-Nitrobenzenediazonium nitrate

[42238-29-9] **$C_6H_4N_4O_5$**



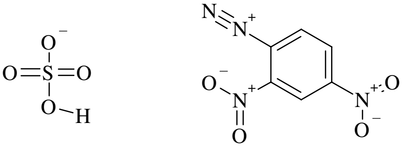
Bamberger, E., *Ber.*, 1895, **28**, 239

The isolated dry salt explodes on heating, but not on friction.

See other DIAZONIUM SALTS

2199. 2,4-Dinitrobenzenediazonium hydrogen sulfate

[64445-49-4] **$C_6H_4N_4O_8S$**

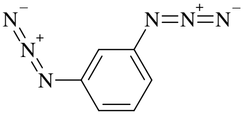


See entry DIAZONIUM SULFATES

See other POLYNITROARYL COMPOUNDS

2200. 1,3-Diazidobenzene

[13556-50-8] **$C_6H_4N_6$**



Acids

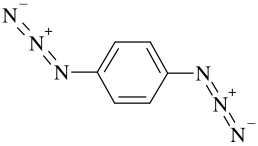
Forster, M. O. *et al., J. Chem. Soc.*, 1907, **91**, 1953

The diazide ignites and explodes mildly with concentrated acid.

See other ORGANIC AZIDES

2201. 1,4-Diazidobenzene

[2294-47-5] **$C_6H_4N_6$**



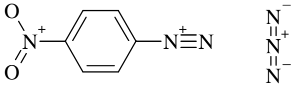
Griess, P., *Ber.*, 1888, **21**, 1561

The diazide explodes very violently on heating.

See other ORGANIC AZIDES

2202. 4-Nitrobenzenediazonium azide

[ ] $C_6H_4N_6O_2$



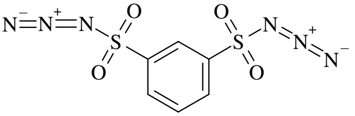
1. Hantzsch, A., *Ber.*, 1903, **36**, 2058
2. Editor's comment, 2005

The dry azide salt exploded violently with a brilliant flash [1]. Subsequent reports claim it impossible to isolate arenediazonium azides, the attempt giving usually the aryl azide or, under very specific conditions, some arylpentazole. Hantzsch had considered both possibilities and produced qualitative evidence against them. He started from the nominal diazonium hydroxide in dry ether, an unusual azo-coupling method. Whatever he got appeared to revert to the diazonium hydroxide on treatment with alkali [2].

See other DIAZONIUM SALTS, NON-METAL AZIDES

2203. Benzene-1,3-bis(sulfonyl azide)

[4547-69-7] $C_6H_4N_6O_4S_2$



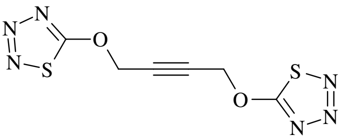
Balabanov, G. P. *et al., Chem. Abs.*, 1969, **70**, 59427

The title compound was the most explosive of a series of 7 substituted benzenesulfonyl azides.

See other ACYL AZIDES

2204. 1,4-Di(1,2,3,4-thiatriazol-5-yloxy)but-2-yne (5,5'-[2-butyne-1,4-diylbis(oxy)]-bis-1,2,3,4-thiatriazole)

[141462-00-2] $C_6H_4N_6O_2S_2$

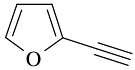


Banert, K. *et al., Angew. Chem. (Int.)*, 1992, **31**(7), 866

An explosive crystalline solid.

See other ACETYLENIC COMPOUNDS, N—S COMPOUNDS, THIATRIAZOLES

2205. 2-Ethynylfuran
[18649-64-4] **C_6H_4O**



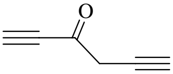
Alone, or Nitric acid

Dunlop, 1953, 77

It explodes on heating or in contact with conc. nitric acid.

See other ACETYLENIC COMPOUNDS

2206. 1,5-Hexadiyn-3-one
[66737-76-6] **C_6H_4O**

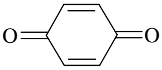


Dowd, P. *et al., Synth. Commun.*, 1978, **8**, 20

The reactive material should be vacuum distilled at ambient temperature to prevent the near-explosive decomposition which occurs if it is heated.

See other ACETYLENIC COMPOUNDS

2207. 1,4-Benzoquinone (Cyclohexadiene-1,4-dione)
[106-51-4] **$C_6H_4O_2$**



Anon., *Loss Prev. Bull.*, 1977, (013), 4

Drums containing moist quinone self-heated, generating smoke and internal pressure. Investigation showed that the moist material showed an exotherm at 40—50°C and decomposed at 60—70°C, possibly owing to presence of impurities. Drums exposed to direct sunlight soon attain a surface temperature of 50—60°C.

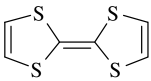
See other SELF-HEATING AND IGNITION INCIDENTS

Other reactants

Yoshida, 1980, 102

MRH values calculated for 13 combinations with oxidants are given.

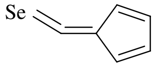
2208. 2,2'-Bi-1,3-dithiole (1,4,5,8-Tetrahydro-1,4,5,8-tetrathiafulvalene)
[31366-25-3] **$C_6H_4S_2$**



Preparative hazard

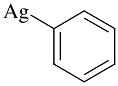
See 1,3-Dithiolium perchlorate

2209. 6-Fulvenoselone
[72443-10-8] **C_6H_4Se**



Schulz, R. *et al., Angew. Chem. (Intern. Ed.)*, 1980, **19**, 69
It polymerises explosively at —196°C.
See other POLYMERISATION INCIDENTS

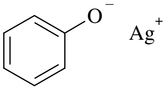
2210. Phenylsilver
[5274-48-6] **C_6H_5Ag**



1. Houben-Weyl, 1970, Vol. 13.1, 774
2. Krause, E. *et al., Ber.*, 1923, **56**, 2064

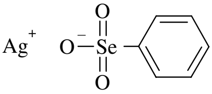
The dry solid explodes on warming to room temperature, or on light friction or stirring [1]. It is more stable wet with ether [2].
See other ARYLMETALS, SILVER COMPOUNDS

2211. Silver phenoxide
[61514-68-9] **C_6H_5AgO**



Macomber, R. S. *et al., Synth. React. Inorg. Met.-Org. Chem.*, 1977, **7**, 111—122
The dried solid product from interaction of lithium phenoxide and silver perchlorate in benzene (probably largely silver phenoxide) exploded on gentle heating. Other silver alkoxide derivatives were unstable.
See Silver perchlorate
See other SILVER COMPOUNDS

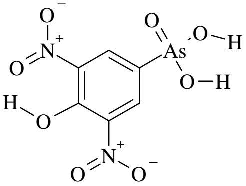
2212. Silver benzeneselenonate
[39254-49-4] **$C_6H_5AgO_3Se$**



See Benzeneselenonic acid
See other SILVER COMPOUNDS

2213. 4-Hydroxy-3,5-dinitrobenzenearsonic acid

[6269-50-7] **$C_6H_5AsN_2O_8$**



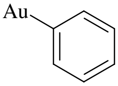
Phillips, M. A., *Chem. & Ind.*, 1947, 61

A heated, unstirred water-wet sludge of this analogue of picric acid exploded violently, apparently owing to local overheating in the containing flask.

See other ORGANIC ACIDS, POLYNITROARYL COMPOUNDS

2214. Phenylgold

[ ] **C_6H_5Au**



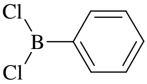
De Graaf, P. W. J. *et al., J. Organomet. Chem.*, 1977, **141**, 353

The impure solid at —70°C exploded when touched with a spatula.

See other ARYLMETALS, GOLD COMPOUNDS

2215. Dichlorophenylborane

[873-51-8] **$C_6H_5BCl_2$**



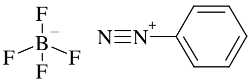
Gerwantch, U. W. *et al., Inorg. Synth.*, 1983, **22**, 207

It is pyrophoric when hot, and extremely sensitive to hydrolysis.

See related ALKYLHALOBORANES

2216. Benzenediazonium tetrafluoroborate

[369-57-3] **$C_6H_5BF_4N_2$**

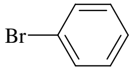


Caesium fluoride, Difluoroamine

See Difluoramine: Benzenediazonium tetrafluoroborate, etc.

See other DIAZONIUM TETRAHALOBORATES

2217. Bromobenzene
[108-86-1] **C_6H_5Br**

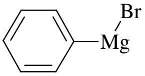


HCS 1980, 667

Bromobutane, Sodium
See Sodium: Halocarbons (reference 7)

Other reactants
Yoshida, 1980, 323
MRH values calculated for 13 combinations with oxidants are given.
See other HALOARYL COMPOUNDS

2218. Phenylmagnesium bromide
[100-58-3] **C_6H_5BrMg**

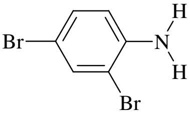


Chlorine
See Chlorine: Phenylmagnesium bromide

Hexafluoropropene
See Hexafluoropropene: Grignard reagents

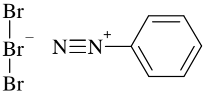
Water
Wosnick, J., INTERNET, 1996
An overconcentrated ether solution of the reagent was poured down a sink. Reaction was violent.
See other GRIGNARD REAGENTS

2219. 2,4-Dibromoaniline
[615-57-6] **$C_6H_5Br_2N$**



Energy of decomposition (in range 150—310°C) measured as 0.24 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other HALOANILINES

2220. Benzenediazonium tribromide
[19521-84-7] **$C_6H_5Br_3N_2$**

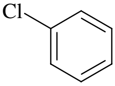


Sorbe, 1968, 40

An explosive compound.

See other DIAZONIUM SALTS

2221. Chlorobenzene
[108-90-7] **C_6H_5Cl**



Other reactants

Yoshida, 1980, 113

MRH values calculated for 13 combinations, largely with oxidants, are given.

Phosphorus trichloride, Sodium

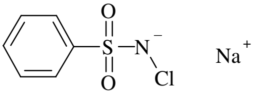
See Sodium: Chlorobenzene, etc.

Sodium

See Sodium: Halocarbons (reference 8)

See other HALOARYL COMPOUNDS

2222. Sodium *N*-chlorobenzenesulfonamide (‘Chloramine B’)
[127-52-6] **$C_6H_5ClNNaO_2S$**

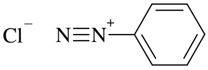


Piotrowski, T., *Chem. Abs.*, 1984, **101**, 60040

In a study of explosive potential of 20 pharmaceutical products, ‘Chloramine B’ was found to present the greatest fire hazard, decomposing explosively at 185°C.

See other N-HALOGEN COMPOUNDS, N-METAL DERIVATIVES

2223. Benzenediazonium chloride
[100-34-5] **$C_6H_5ClN_2$**

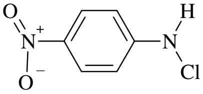


1. Hantzsch, A. *et al., Ber.*, 1901, **34**, 3338
2. Grewer, T., *Chem. Ing. Tech.*, 1975, **47**, 233—234
3. See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

The dry salt was more or less explosive, depending on the method of preparation [1]. DTA examination of a 15% solution of the diazonium salt in hydrochloric acid showed an exothermic decomposition reaction with the exotherm peak at 65°C. Adiabatic decompositon of the solution at 20°C took 80 min to attain the maximum temperature of 80°C [2]. The heat of decomposition Q was determined as 1.5 kJ/g [3].
See Benzenediazonium tetrachlorozincate

Potassium *O*-methyldithiocarbonate
See Thiophenol,
See also DIAZONIUM SULFIDES AND DERIVATIVES
See other DIAZONIUM SALTS

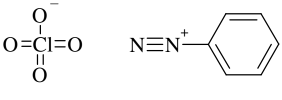
2224. *N*-Chloro-4-nitroaniline
[59483-61-3] **$C_6H_5ClN_2O_2$**



1. Goldschmidt, S. *et al., Ber.*, 1922, **55**, 2450
2. Pyetlewski, L. L., *Rept. AD A028841*, 24, Richmond (Va.), NTIS, 1976

Though stable at —70°C, it soon decomposes explosively at ambient temperature [1], and violently on heating slightly [2].
See other N-HALOGEN COMPOUNDS, NITROARYL COMPOUNDS

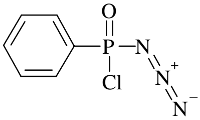
2225. Benzenediazonium perchlorate
[114328-95-9] **$C_6H_5ClN_2O_4$**



Alone, or Sulfuric acid
1. Vorlander, D., *Ber.*, 1906, **39**, 2713—2715
2. Hofmann, K. A. *et al., Ber.*, 1906, **39**, 3146—3148

The salt explodes on friction, impact or contact with sulfuric acid when still wet with liquor [1], and is frightfully explosive when dry [2].
See other DIAZONIUM PERCHLORATES

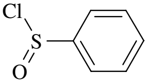
2226. Phenylphosphonic azide chloride (Phenylphosphonazidic chloride)
[4129-46-8] **$C_6H_5ClN_3OP$**



Utvary, K., *Inorg. Nucl. Chem. Lett.*, 1965, **1**, 77—78
A violent explosion occurred during distillation at 80—88°C/0.46 mbar of mixtures containing the azide chloride and the diazide
See Phenylphosphonic diazide
See other ACYL AZIDES

2227. Benzenesulfinyl chloride

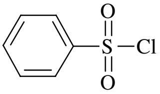
[4972-29-6] **C_6H_5ClOS**



Anon., *Chem. Eng. News*, 1957, **35**, 57
A glass bottle, undisturbed for several months, exploded, probably from internal gas pressure arising from photolytic or hydrolytic decomposition.
See other ACYL HALIDES, GAS EVOLUTION INCIDENTS

2228. Benzenesulfonyl chloride

[98-09-9] **$C_6H_5ClO_2S$**



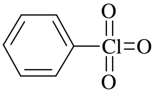
HCS 1980, 188

Anon., *Chem. Eng. News*, 1957, **35**(47), 57
A glass container exploded after shelf storage for several months, (probably from internal gas pressure arising from slow hydrolysis by atmospheric or adsorbed moisture).
See other GAS EVOLUTION INCIDENTS

Dimethyl sulfoxide
See Dimethyl sulfoxide: Acyl halides
See other ACYL HALIDES

2229. Perchlorylbenzene

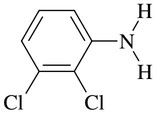
[5390-07-8] **$C_6H_5ClO_3$**



Aluminium chloride
Bruce, W. F., *Chem. Eng. News*, 1960, **38**(4), 63
A mixture is quiescent for some time, then suddenly explodes. Many perchloryl aromatics appear to be inherently shock-sensitive.
See other PERCHLORYL COMPOUNDS

2230. 2,3-Dichloroaniline

[608-27-5] **$C_6H_5Cl_2N$**



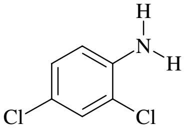
T_{ait24} was determined as 212°C by adiabatic Dewar tests, with an apparent energy of activation of 119 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other HALOANILINES

2231. 2,4-Dichloroaniline

[554-00-7] **$C_6H_5Cl_2N$**



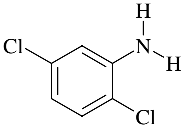
T_{ait24} was determined as 211°C by adiabatic Dewar tests, with an apparent energy of activation of 129 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other HALOANILINES

2232. 2,5-Dichloroaniline

[95-82-9] **$C_6H_5Cl_2N$**



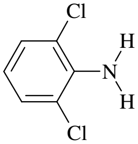
T_{ait24} was determined as 216°C by adiabatic Dewar tests, with an apparent energy of activation of 126 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other HALOANILINES

2233. 2,6-Dichloroaniline

[608-31-1] **$C_6H_5Cl_2N$**



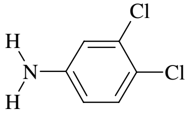
T_{ait24} was determined as 217°C by adiabatic Dewar tests, with an apparent energy of activation of 227 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other HALOANILINES

2234. 3,4-Dichloroaniline

[95-76-1] **$C_6H_5Cl_2N$**



HCS 1980, 374

T_{ait24} was determined as 187°C by adiabatic Dewar tests, with an apparent energy of activation of 146 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Preparative hazard

Kotoyori, T., private comm., 1983

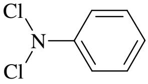
During pilot-scale vacuum distillation from a mild steel still of the crude hydrogenation product of 3,4-dichloronitrobenzene, normal conditions had been established as 160—170°C/43—63 mbar with steam heating at 194°C. While the seventh 8 t batch was being distilled, distillation conditions were 187°C/135 mbar, and later 194°C/165 mbar, at which point heating was stopped but the temperature and pressure kept rising. The vessel (without a pressure relief) was isolated for 2.5 h while the vacuum line was examined for blockage. Before vacuum could be reapplied, the vessel ruptured at the lid flange with eruption of white smoke and black tar. Several contributory factors for the decomposition were established later. 3,4-Dichloroaniline undergoes dehydrochlorination-polymerisation reactions, forming hydrochloride salts, at temperatures above 180°C in presence of ferric chloride, and the salts dissociate above 260°C with violent liberation of hydrogen chloride gas. Leaks of water into the still from a condenser, and of air from a hardened and cracked gasket, tended to increase the rate of formation of ferric chloride by hydrolysis of the aniline and oxidation of iron dissolved from the vessel, as well as causing increases in distillation temperature and pressure. The level of dissolved iron in the residue after the accident was around 1% (80 kg Fe), owing to the fact that distillation residues were not removed after each batch was completed. Recommended precautionary measures included fitting a pressure relief, distilling under alkaline conditions, better gasket maintenance to prevent air leaks, and removal of the residue after each batch.

See 3,4-Dichlorophenylhydroxylamine

See other HALOANILINES

2235. ***N,N*****-Dichloroaniline**

[70278-00-1] **$C_6H_5Cl_2N$**



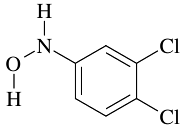
Goldschmidt, S., *Ber.*, 1913, **46**, 2732

The oil prepared at —20°C explodes while warming to ambient temperature.

See other N-HALOGEN COMPOUNDS

2236. 3,4-Dichlorophenylhydroxylamine

[33175-34-7] **$C_6H_5Cl_2NO$**



1. Tong, W. R. *et al., Loss Prev.*, 1977, **11**, 71—75
2. MacNab, J. I., *Runaway Reactions*, 1981, 3/S, 1—12

A violent explosion during the plant-scale catalytic hydrogenation of 3,4-dichloronitrobenzene to the aniline (heat of hydrogenation is 523 kJ/mol, 2.72 kJ/g) was traced to thermal decomposition of one of the reaction intermediates, 3,4-dichlorophenylhydroxylamine. The latter is normally present to the extent of about 5%, but contamination of the nitro compound by unseparated wash-water containing 2% of nitrite ion had slowed the reaction and increased the proportion of hydroxylamine to 35%. Investigation of the thermal stability of the reaction mixture as hydrogenation proceeded showed that the minimum autodecomposition temperature of 260°C coincided with the maximum concentration of the hydroxylamine at 60% of the theoretical hydrogen uptake. The pure hydroxylamine begins to decompose at 80°C. Shortly before the explosion occurred, the heat input had been increased to offset the slower reaction rate and had triggered the decomposition. The sequence was confirmed experimentally, and maximum rates of increase of 6.7°C/s and 36 bar/s were recorded for the decomposition [1]. The intial temperature for exothermic decomposition of this reduction intermediate, alone or diluted with the nitro or amino compounds, was 80°C or below, with exotherms up to 60°C [2].

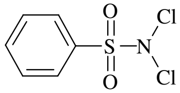
See 2-Chloro-5-methylphenylhydroxylamine

See also 3,4-Dichloroaniline

See other CATALYTIC NITRO REDUCTION PROCESSES, N—O COMPOUNDS

2237. ***N,N*****-Dichlorobenzenesulfonamide**

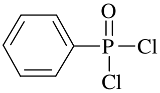
[473-34-7] **$C_6H_5Cl_2NO_2S$**



Energy of decomposition (in range 160—260°C) measured as 0.92 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other N-HALOGEN COMPOUNDS

2238. Phenylphosphonyl dichloride

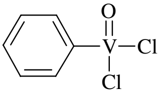
[824-72-6] **$C_6H_5Cl_2OP$**



Koch-Light Ltd., private comm., 1976
A bottle of the dichloride exploded violently while on a bench. No cause was established, but diffusive ingress of moisture, or an intramolecular Friedel-Crafts reaction, both of which would form free hydrogen chloride, seem possible contributory factors.
See related ACYL HALIDES, NON-METAL HALIDES

2239. Phenylvanadium(V) dichloride oxide

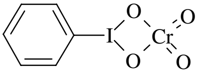
[28597-01-5] **$C_6H_5Cl_2OV$**



Houben-Weyl, 1975, Vol. 13.3, 365
Thermal decomposition may be explosive.
See related ARYLMETALS, METAL HALIDES

2240. Phenyliodine(III) chromate ('[(Chromyldioxy)iodo]benzene')

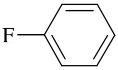
[ ] **$C_6H_5CrIO_4$**



Sidgwick, 1950, 1250
It explodes at 66°C.
See other IODINE COMPOUNDS

†2241. Fluorobenzene

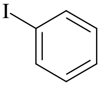
[462-06-6] **C_6H_5F**



See other HALOARYL COMPOUNDS

2242. Iodobenzene

[591-50-4] **C_6H_5I**



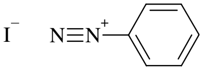
Sorbe, 1968, 66

It explodes on heating above 200°C.

See other HALOARYL COMPOUNDS, IODINE COMPOUNDS

2243. Benzenediazonium iodide

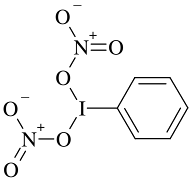
[57965-32-9] **$C_6H_5IN_2$**



See entry DIAZONIUM SALTS, DIAZONIUM TRIIODIDES

2244. Phenyliodine(III) nitrate

[58776-08-2] **$C_6H_5IN_2O_6$**



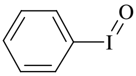
Sorbe, 1968, 66

It explodes above 100°C.

See other IODINE COMPOUNDS

2245. Iodosylbenzene

[536-80-1] **C_6H_5IO**



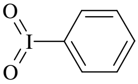
1. Saltzman, A. *et al., Org. Synth.*, 1963, **43**, 60
2. Banks, D. F., *Chem. Rev.*, 1966, **66**, 255

It explodes at 210°C [1], and homologues generally explode on melting [2].

See other IODINE COMPOUNDS

2246. Iodylbenzene

[696-33-3] **$C_6H_5IO_2$**



1. Sharefkin, J. G. *et al., Org. Synth.*, 1963, **43**, 65
2. Banks, D. F., *Chem. Rev.*, 1966, **66**, 259

It explodes at 230°C [1]. Extreme care should be used in heating, compressing or grinding iodyl compounds, as heat or impact may cause detonation of homologues [2].

See other IODINE COMPOUNDS

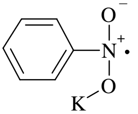
2247. Benzenediazonium triiodide

[68596-95-2] **$C_6H_5I_3N_2$**

See entry DIAZONIUM TRIIODIDES

2248. Potassium nitrobenzene

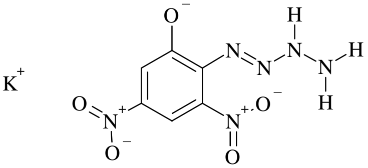
[ ] **$C_6H_5KNO_2$**



See entry NITROAROMATIC—ALKALI HAZARDS; Potassium radical salts

2249. Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide

[70324-35-5] **$C_6H_5KN_6O_5$**



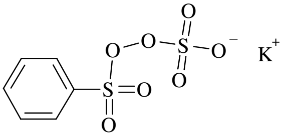
Kenney, J. F., US Pat. 2 728 760, 1952

It is explosive.

See other HIGH-NITROGEN COMPOUNDS, POLYNITROARYL COMPOUNDS

2250. Potassium benzenesulfonylperoxosulfate

[ ] **$C_6H_5KO_7S_2$**



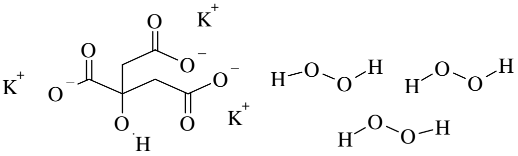
Davies, 1961, 65

It explodes on friction or warming.

See other DIACYL PEROXIDES

2251. Potassium citrate tri(hydrogen peroxidate)

[31226-90-1] **$C_6H_5K_3O_7.3H_2O_2$**



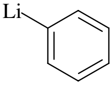
Anon., *Jahresber.*, 1978, 75

Treatment of the citrate monohydrate with a 20% excess of 70% hydrogen peroxide gave a crystalline product which, after vacuum drying at 50°C corresponded approximately to the tri(hydrogen peroxidate). It decomposed violently when disturbed with a porcelain spatula.

See other CRYSTALLINE HYDROGEN PEROXIDATES

2252. Phenyllithium

[591-51-5] **C_6H_5Li**



Preparative hazard

See Lithium: Bromobenzene

Titanium tetraethoxide

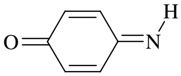
Gilman, H. *et al., J. Org. Chem.*, 1945, **10**, 507

The product of interaction at 0°C (of unknown composition) ignited in air and reacted violently with water.

See other ARYLMETALS

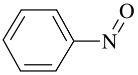
2253. 1,4-Benzoquinone monoimine (2,5-Cyclohexadienone-4-imine)

[3009-34-5] **C_6H_5NO**



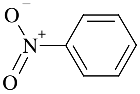
Willstätter, R. *et al., Ber.*, 1906, **37**, 4607
The solid decomposes with near-explosive violence.
See related DIENES

2254. Nitrosobenzene
[586-96-9] **C_6H_5NO**



Energy of decomposition (in range 190—380°C) measured as 0.823 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other NITROSO COMPOUNDS

2255. Nitrobenzene
[98-95-3] **$C_6H_5NO_2$**



(*MCA SD-21*, 1967); *HCS 1980*, 681; 32RSC Lab Hazards Data Sheet No. 77, 1988

1. *CHETAH*, 1990, 182
2. It is marginally detonable; requiring a 50 g tetryl booster.

The heat of decomposition of nitrobenzene was determined (360—490°C) as 1.76 kJ/g by DSC, and T_{ait24} was as 280°C by adiabatic Dewar tests, with an apparent energy of activation of 216 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkali

1. Hatton, J. P., private comm., 1976
2. Anon., *Sichere Chemiearb.*, 1975, **27**, 89; Bilow, W., private comm., 1976
3. Wohl, A., *Ber.*, 1899, **32**, 3846; 1901, **34**, 2444
4. Anon., *ABCM Quart. Safety Summ.*, 1953, **24**, 42
5. Bretherick, L., *Chem. & Ind.*, 1976, 576
6. *CHSO Rept. Y4648-181*, Washington (DC), OSHA, 1981

Heating a mixture of nitrobenzene, flake sodium hydroxide and a little water in an autoclave led to an explosion [1]. During the technical-scale preparation of a warm solution of nitrobenzene in methanolic potassium hydroxide (flake 90% material), accidental omission of most of the methanol led to an accelerating exothermic reaction which eventually ruptured the 6 m^3 vessel. Laboratory investigation showed that no exothermic reaction occurred between potassium hydroxide and nitrobenzene, either alone, or with the full amount (3.4 vol.) of methanol, but that it did if only a little methanol were present. The residue was largely a mixture of azo- and azoxy-benzene [2]. The violent conversion of nitrobenzene to (mainly) 2-nitrophenol by heating with finely powdered and anhydrous potassium hydroxide had been described earlier [3]. Accidental substitution of

nitrobenzene for aniline as diluent during large-scale fusion of benzanthrone with potassium hydroxide caused a violent explosion [4]. Related incidents involving aromatic nitro compounds and alkali are also discussed [5]. Drying wet nitrobenzene in presence of flake sodium hydroxide (probably by distilling out the nitrobenzene—water azeotrope) led to separation of finely divided solid base which remained in contact with the hot dry nitrobenzene under essentially adiabatic conditions. A violent explosion subsequently blew out a valve and part of the 10 cm steel pipeline. These conditions, when simulated in an ARC test run, also led to thermal runaway and explosion [6].
See other NITROAROMATIC—ALKALI HAZARDS

Aluminium chloride
See Aluminium chloride: Nitrobenzene, or :Nitrobenzene, Phenol

Aniline, Glycerol, Sulfuric acid
See Quinoline

Other reactants
Yoshida, 1980, 277
MRH values calculated for 2 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Dinitrogen tetraoxide: Nitrobenzene	
Fluorodinitromethane: Nitrobenzene	
Nitric acid: Nitroaromatics, or: Nitrobenzene	
Peroxodisulfuric acid: Organic liquids	
Sodium chlorate: Nitrobenzene	MRH 4.94/12
Tetranitromethane: Aromatic nitro compounds	MRH 7.36/76
Uronium perchlorate: Organic materials	

Phosphorus pentachloride
See Phosphorus pentachloride: Nitrobenzene

Potassium
See Potassium: Nitrogen-containing explosives

Sulfuric acid
1. *MCA Case History No. 678*
2. Silverstein, J. L. *et al., Loss Prev.*, 1981, **14**, 78

Nitrobenzene was washed with dilute (5%) sulfuric acid to remove amines, and became contaminated with some tarry emulsion that had formed. After distillation, the hot tarry acidic residue attacked the iron vessel with hydrogen evolution, and an explosion eventually occurred. It was later found that addition of the nitrobenzene to the diluted acid did not give emulsions, while the reversed addition did. A final wash with sodium carbonate solution was added to the process [1]. During hazard evaluation of a continuous adiabatic process for manufacture of nitrobenzene, it was found that the latter with 85% sulfuric acid gave a violent exotherm above 200°C, and with 69% acid a mild exotherm at 150—170°C [2].

Sulfuric acid, Sulfur trioxide
See 3-Nitrobenzenesulfonic acid

Tin(IV) chloride

Unpublished observations, 1948

Mixtures of nitrobenzene and tin(IV) chloride undergo exothermic decomposition with gas evolution above 160°C.

See other GAS EVOLUTION INCIDENTS, NITROARYL COMPOUNDS

2256. 2-Nitrosophenol (1,2-Benzoquinone monoxime)
[13168-78-0] ([637-62-7]) $C_6H_5NO_2$

Energy of decomposition (in range 80—320°C) measured as 1.214 kJ/g by DSC, and T_{ait24} was determined as the very low figure of 53°C by adiabatic Dewar tests, with an apparent energy of activation of 462 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other DEFLAGRATION INCIDENTS

Alone, or Acids

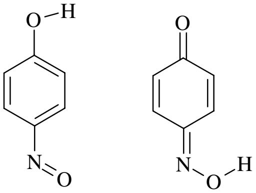
Baeyer, A. *et al., Ber.*, 1902, **35**, 3037

It explodes on heating or in contact with concentrated acids (the latter possibly involving Beckmann rearrangement and/or polymerisation of the oxime form, which is effectively a 1,3-diene).

See other NITROSO COMPOUNDS, OXIMES

See related DIENES

2257. 4-Nitrosophenol (1,4-Benzoquinone monoxime)
[637-62-7] ([104-91-6]) $C_6H_5NO_2$



Alone, or Acids, or Alkalies

1. Milne, W. D., *Ind. Eng. Chem.*, 1919, **11**, 489
2. Kuznetsov, V., *Chem. Abs.*, 1940, **34**, 3498i
3. Anon., *Sichere Chemiearb.*, 1980, 3532, 6
4. Klais, O. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C24—C34, Rugby, IChE, 1983
5. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987

Stored barrels heated spontaneously and caused a fire. Contamination of the bulk material by acid or alkali may cause ignition [1]. The tendency to spontaneous ignition was found to be associated with the presence of nitrates in the sodium nitrite used in preparation. A diagnostic test for this tendency is to add sulfuric acid, when impure material will effervesce or ignite. The sodium salt is more suitable for storage purposes [2] (*but see* Sodium 4-nitrosophenoxide). Compressed material has a greater tendency to self-ignition than the loose solid, and a 20—30 kg quantity of centrifuged material ignited in a drum located near a steam heater [3]. Material for laboratory use is now supplied wet with 30—40% water. The heat of decomposition was determined as 1.2 kJ/g, and the pressure rise occurring during exothermic decomposition is low [4]. However, the deflagration rate for the solid of 8 cm/min is relatively high [5].

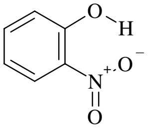
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

See other NITROSO COMPOUNDS

See related OXIMES

2258. 2-Nitrophenol

[88-75-5] **$C_6H_5NO_3$**



Energy of decomposition (in range 260—365°C) measured as 2.15 kJ/g by DSC, and T_{ait24} was determined as 182°C by adiabatic Dewar tests, with an apparent energy of activation of 135 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Chlorosulfuric acid

See 4-Hydroxy-3-nitrobenzenesulfonyl chloride

Potassium hydroxide

491M, 1975, 342

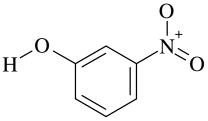
The molten phenol reacts violently with commercial 85% potassium hydroxide pellets (possibly involving formation of the *aci-o*-nitroquinonoid salt).

See NITROAROMATIC—ALKALI HAZARDS

See other NITROARYL COMPOUNDS

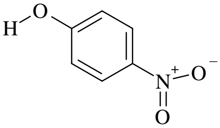
2259. 3-Nitrophenol

[554-84-7] **$C_6H_5NO_3$**



T_{ait24} was determined as 213°C by adiabatic Dewar tests, with an apparent energy of activation of 148 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other NITROARYL COMPOUNDS

2260. 4-Nitrophenol
[100-02-7] **$C_6H_5NO_3$**



HCS 1980, 688

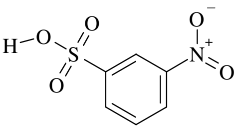
1. Grewer. T. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 657—664, Basle, SSCI, 1980
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

There is a high rate of pressure increase during exothermic decomposition [1]. Energy of decomposition (in range 240—440°C) measured as 1.58 kJ/g by DSC, and T_{ait24} was determined as 185°C by adiabatic Dewar tests, with an apparent energy of activation of 117 kJ/mol [2].

Diethyl phosphite
See Diethyl phosphite: 4-Nitrophenol

Potassium hydroxide
Solid mixtures of 4-nitrophenol with potassium hydroxide (1:1.5 mol) readily deflagrate, at the rapid rate of 30 cm/min.
See Potassium 4-nitrophenoxide
See entry METAL NITROPHENOXIDES, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 3)
See other DEFLAGRATION INCIDENTS, NITROARYL COMPOUNDS

2261. 3-Nitrobenzenesulfonic acid
[98-47-5] **$C_6H_5NO_5S$**



Sulfuric acid, Sulfur trioxide
1. *MCA Case History No. 1482*
2. *MCA Case History No. 944*
3. *See entry* SELF-ACCELERATING REACTIONS

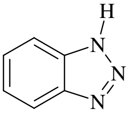
4. Nolan, 1983, Case history 102
5. Bergroth, K., *Loss Prev. Bull.*, 1993, (109), 1

The acid is prepared by sulfonation of nitrobenzene with oleum, and the reaction product consists essentially of a hot solution of the acid in sulfuric acid. A completed 270 l batch exploded violently after hot storage at ~150°C for several hours. An exotherm develops at 145°C, and the acid is known to decompose at ~200°C [1]. A similar incident arose from water leaking from a cooling coil into the fuming sulfuric acid reaction medium, which caused an exotherm to over 150°C and subsequent violent decomposition [2]. Detailed examination of the thermal decomposition of the acid shows that it is much slower for the isolated acid than for the reaction mass, and that the concentration of sulfur trioxide in the oleum used for sulfonation bears directly upon the decomposition rate. Care must be exercised when interpreting short-term DSC test results, because the self-acceleration features are not immediately evident. A Q value of 1 kJ/g of reaction mass after sulfonation with 25% oleum was found experimentally [3]. A 2000 l batch of the acid prepared with 20% excess of 65% oleum had been cooled to 70°C prior to being blown over into a tank for treatment with sodium carbonate. Application of air pressure at 2.75 bar to the reactor failed to transfer the product, so the transfer lines were isolated and steamed at 2 bar to clear them. On reconnecting the lines, the condensed water reacted with the excess oleum, leading to exothermic decomposition of the acid, rupture of the vessel and a fire [4]. An explosion in a plant resulted because of crystallisation from the oleum sulfonation mixture in a control valve, which failed. Manual operation led to steam flowing back from the quench to a nitration-product holding tank, which overheated and exploded [5].

See other NITROARYL COMPOUNDS, ORGANIC ACIDS, SULFONATION INCIDENTS

2262. Benzotriazole

[95-14-7] **$C_6H_5N_3$**



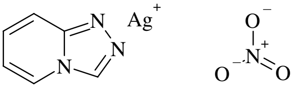
1. Anon., *Chem. Eng. News*, 1956, **34**, 2450
2. *CHETAH*, 1990, 182
3. Stull, 1977, 22—23

A 1 t batch decomposed exothermally, then detonated at 220°C, during distillation at 160°C/2.5 mbar. No cause was found, and similar batches had previously distilled satisfactorily. The multiple N—N bonding would tend to cause instability in the molecule, particularly in presence of heavy metals, but these were absent in this case [1]. It is shock sensitive (probably not very) [2]. Benzotriazole is an endothermic compound (ΔH_f° (s) +249.8 kJ/mol, 2.1 kJ/g) and this energy on release would attain an adiabatic decomposition temperature approaching 1100°C, with an 18 bar pressure increase in the closed system [3].

See other ENDOTHERMIC COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

2263. 1,2,4-Triazolo[4,3-*a*]pyridine silver nitrate

[274-80-6] free base **$C_6H_5N_3.AgNO_3$**



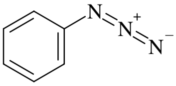
Fargher, R. G. *et al., J. Chem. Soc.*, 1915, **107**, 696

The base [274-80-6] forms an addition compound with silver nitrate which decomposes at 228°C in a m.p. capillary, but explodes when heated in larger amount.

See other AMMINEMETAL NITRATES, SILVER COMPOUNDS

2264. Phenyl azide (Azidobenzene)

[622-37-7] **$C_6H_5N_3$**



1. Lindsay, R. O. *et al., Org. Synth.*, 1955, Coll. Vol. 3, 710
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
3. Lee, S. W. *et al., Inorg. Chem.*, 1988, **27**, 1213—1219

Though distillable at considerably reduced pressure, phenyl azide explodes when heated at ambient pressure, and occasionally at lower pressures [1]. The energy of decomposition has been determined (130—260°C) as 1.36 kJ/g by DSC, and T_{ait24} was determined as 87°C by adiabatic Dewar tests, with an apparent energy of activation of 119 kJ/mol [2]. It is best stored as a 3M solution in toluene. Exposure to heavy metals should be avoided [3].

Lewis acids

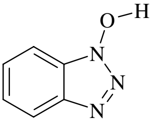
Boyer, J. H. *et al., Chem. Rev.*, 1954, **54**, 29

The ready decomposition of most aryl azides with sulfuric acid and Lewis acids may be vigorous or violent, depending on structure and conditions. In absence of a diluent (carbon disulfide), phenyl azide and aluminium choride exploded violently.

See other ORGANIC AZIDES

2265. 1-Hydroxybenzotriazole

[2592-95-2] **$C_6H_5N_3O$**



Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 52—53

A sample of the compound (which can isomerise to two *N*-oxide forms) was inadvertently heated, probably to well over 160°C, during vacuum drying and exploded violently. Several salts have been reported as powerfully explosive.

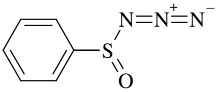
Copper(II) nitrate

See Copper(II) nitrate: Hydroxybenzotriazole, Ethanol

See other HIGH-NITROGEN COMPOUNDS, N—O COMPOUNDS, TRIAZOLES

2266. Benzenesulfinyl azide

[21230-20-6] **$C_6H_5N_3OS$**

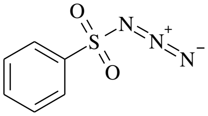


See entry SULFINYL AZIDES

See other ACYL AZIDES

2267. Benzenesulfonyl azide

[938-10-3] **$C_6H_5N_3O_2S$**



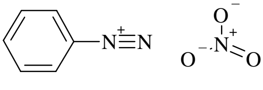
Dermer, O. C. *et al., J. Amer. Chem. Soc.*, 1955, **77**, 71

Whereas the pure azide decomposes rapidly but smoothly at 105°C, the crude material explodes violently on heating.

See other ACYL AZIDES

2268. Benzenediazonium nitrate

[619-97-6] **$C_6H_5N_3O_3$**

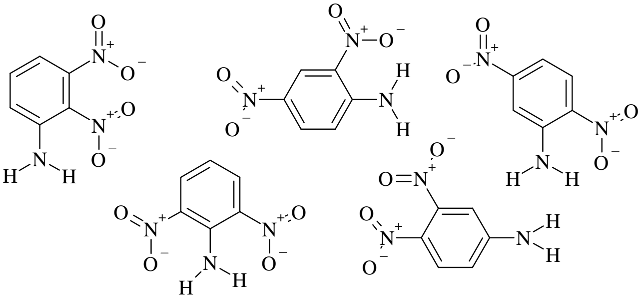


1. Urbanski, 1967, Vol. 3, 201
2. Stull, 1977, 19

Although not a practical explosive, the isolated salt is highly sensitive to friction and impact, and explodes at 90°C [1]. It is, like most diazonium salts, endothermic, with ΔH_f° (s) +200.8 kJ/mol, 1.2kJ/g [2].

See other DIAZONIUM SALTS, ENDOTHERMIC COMPOUNDS

2269. Dinitroanilines (: all isomers except 3,5-)
2,3- [602-03-9]; 2,4- [97-02-9]; 2,5- [619-18-1];
2,6- [606-22-4]; 3,4- [610-41-3] **$C_6H_5N_3O_4$**

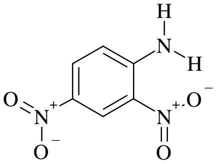


Chlorine, Hydrochloric acid

See Hydrochloric acid: Chlorine, Dinitroanilines

See other POLYNITROARYL COMPOUNDS

2270. 2,4-Dinitroaniline
[97-02-9] **$C_6H_5N_3O_4$**



HCS 1980, 437

Charcoal

Leleu, *Cahiers*, 1980, (99), 278

A mixture with powdered charcoal smoked above 280°C and ignited at 350°C.

See other POLYNITROARYL COMPOUNDS

Preparative hazard

1. Sorbe, 1968, 151
2. *CHETAH*, 1990, 183
3. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

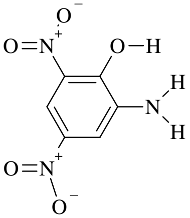
It is a compound with high fire and explosion hazards [1], showing fast flame propagation on heating the powder moderately. Not sensitive to mechanical shock, it can be exploded by a detonator [2]. T_{ait24} was determined as 217°C by adiabatic Dewar tests, with an apparent energy of activation of 129 kJ/mol [3].

See 1-Chloro-2,4-dinitrobenzene: Ammonia

See entry HIGH RATE DECOMPOSITION

2271. 2-Amino-4,6-dinitrophenol

[96-91-3] **$C_6H_5N_3O_5$**



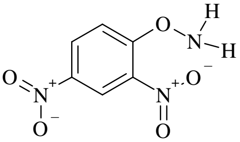
Sorbe, 1968, 152

This partially reduced derivative of picric acid, ‘picramic acid’, explodes very powerfully when dry.

See other POLYNITROARYL COMPOUNDS

2272. *O*-(2,4-Dinitrophenyl)hydroxylamine

[17508-17-7] **$C_6H_5N_3O_5$**



Potassium hydride

Radhakrishna, A. S. *et al., J. Org. Chem.*, 1979, **44**, 4838

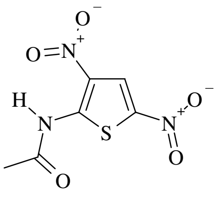
Interaction in THF gives 2,4-dinitrophenol and ammonia, and on one occasion a violent detonation occurred; potassium dinitrophenoxide may have been involved.

See Sodium 2,4-dinitrophenoxide

See other N—O COMPOUNDS, POLYNITROARYL COMPOUNDS

2273a. 2-Acetylamino-3,5-dinitrothiophene

[51249-08-2] **$C_6H_5N_3O_5S$**



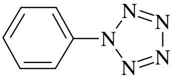
Fast flame propagation on heating the powder moderately.

See entry HIGH RATE DECOMPOSITION

See other POLYNITROARYL COMPOUNDS

2273b. Phenylpentazole

[32785-44-7] **$C_6H_5N_5$**



Ugi, I., *Comprehensive Heterocyclic Chemistry*, (Ed. Katritzky, A. R.), Vol. 5, 843, Oxford, Pergamon, 1984

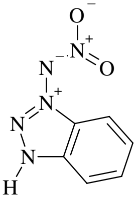
The archetype of the arylpentazoles, the only pentazoles of proven structurre thus far isolated, it is liable to explode above —5°C. Larger and more electron rich analogues are more stable, but still explosive.

See also PENTAZOLES

See other HIGH-NITROGEN COMPOUNDS

2274. Benzotriazolium 1-nitroimidate

[ ] **$C_6H_5N_5O_2$**



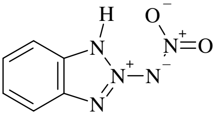
A dangerous impact-sensitive solid which explodes at the m.p., 74°C.

See 1-(Nitroamino)benzotriazole

See entry N-AZOLIUM NITROIMIDATES

2275. Benzotriazolium 2-nitroimidate

[52096-20-5] **$C_6H_5N_5O_2$**

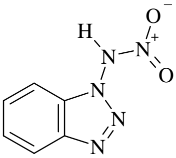


A dangerous solid which explodes at the m.p., 84°C.

See entry N-AZOLIUM NITROIMIDATES

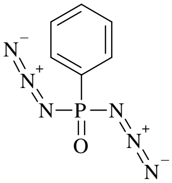
2276. 1-(Nitroamino)benzotriazole

[52096-18-1] **$C_6H_5N_5O_2$**



This is the structure assigned by *chem. Abs.* to the claimed benzotriazolium 1-nitroimidate above. The editor suspects they are right and that the nitroamine structure should also be considered for the 2- isomer. The *aci*-nitro structures are also possible.
See Benzotriazolium 1-nitroimidate
See also N—NITRO COMPOUNDS

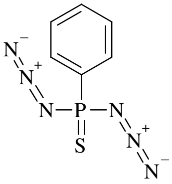
2277. Phenylphosphonic diazide
[4129-28-6] **$C_6H_5N_6OP$**



1. Baldwin, R. A., *J. Org. Chem.*, 1965, **30**, 3866
2. Utvary, K., *Inorg. Nuclear Chem, Lett.*, 1965, **1**(2), 77

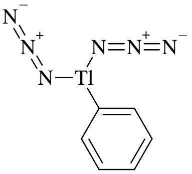
Although a small sample had been distilled at 72—74°C/0.13 mbar without incident, it decomposed vigorously on exposure to flame, and the liquid was impact-sensitive, exploding vigorously. The material can be prepared and handled safely in pyridine solution [1]. Another worker, distilling at slightly higher pressure and 80—4°C, gave up after experiencing an explosion [2].
See other ACYL AZIDES

2278. Phenylthiophosphonic diazide
[ ] **$C_6H_5N_6PS$**



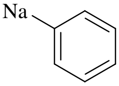
Baldwin, R.A., *J. Org. Chem.*, 1965, **30**, 3866
During an attempt to distil crude material at 80°C/0.13 mbar, a violent explosion occurred. The material can be prepared and handled safely in pyridine solution.
See other ACYL AZIDES

2279. Phenylthallium diazide
[ ] **$C_6H_5N_6Tl$**



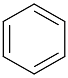
Pascal, 1961, Vol. 6, 1019
It decomposes violently at 200°C.
See related METAL AZIDES

2280. Phenylsodium
[1623-99-0] **C_6H_5Na**



Preparative hazard
Sorbe, 1968, 86
Suspensions containing phenylsodium may ignite and burn violently in moist air.
See Sodium: Halocarbons (reference 8)
See other ARYLMETALS

†2281. Benzene
[71-43-2] **C_6H_6**



(*MCA SD-2*, 1960); *NSC 308*, 1979; *FPA H18*, 1973; *HCS 1980*, 187; *RSC Lab. Hazard Data Sheet No. 20*, 1984

Arsenic pentafluoride, Potassium methoxide
See Arsenic pentafluoride: Benzene, etc.

Diborane
See Diborane: Benzene, etc.

Hydrogen, Raney nickel
Anon., *Loss Prev. Bull.*, 1979, (028), 91—92
Hydrogenation of benzene to cyclohexane was effected in a fixed bed reactor at 210—230°C, but a fall in conversion was apparent. Increasing the bed temperature by 10°C and the hydrogen flow led to a large increase in reaction rate which the interbed cooling coils could not handle, and an exotherm to 280°C developed, with a hot spot of around 600°C which bulged the reactor wall.
See other HYDROGENATION INCIDENTS

Interhalogens MRH value shows % of interhalogen
See Bromine trifluoride: Halogens, etc.
Bromine pentafluoride: Hydrogen-containing materials MRH 3.85/73
Iodine heptafluoride: Organic solvents
Iodine pentafluoride: Benzene

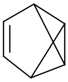
Other reactants
Yoshida, 1980, 334
MRH values calculated for 17 combinations with oxidants are given.

Oxidants MRH values show % of oxidant

See Dioxygen difluoride: Various materials
Dioxygenyl tetrafluoroborate: Organic materials
Nitric acid: Hydrocarbons MRH 8.15/82
Nitryl perchlorate: Organic solvents
Oxygen (Liquid): Hydrocarbons MRH 9.83/75
Ozone: Aromatic compounds, or: Benzene, etc. MRH Benzene12.05/75
Ozone: Aromatic compounds, or: Benzene, etc. MRH Benzene12.05/75
Permanganic acid: Organic materials
Peroxodisulfuric acid: Organic liquids
Peroxomonosulfuric acid: Aromatic compounds
Silver perchlorate MRH 3.51/91
Sodium peroxide: Organic liquids, etc. MRH 2.76/93

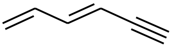
Uranium hexafluoride
See Uranium hexafluoride: Aromatic hydrocarbons

2282. Benzvalene
[659-85-8] **C_6H_6**



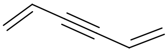
Katz, T. J. *et al., J. Amer. Chem. Soc.*, 1971, **93**, 3782
When isolated, this highly strained valence tautomer of benzene exploded violently when scratched. It may be handled safely in solution in ether.
See other STRAINED-RING COMPOUNDS

2283. 1,3-Hexadien-5-yne
[10420-90-3] **C_6H_6**



Brandsma, 1971, 132
Distillation of this rather unstable material at normal pressure involves risk of an explosion.
See other ALKYNES, DIENES

†2284. 1,5-Hexadien-3-yne (Divinylacetylene)
[821-08-9] **C_6H_6**



1. Nieuwland, J. A. *et al., J. Amer. Chem. Soc.*, 1931, **53**, 4202
2. Cupery, M. E. *et al., J. Amer. Chem. Soc.*, 1934, **56**, 1167—1169

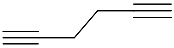
3. Handy, C. T. *et al., J. Org. Chem.*, 1962, **27**, 41

The extreme hazards involved in handling this highly reactive material are stressed. Freshly distilled material rapidly polymerises at ambient temperature to produce a gel and then a hard resin. These products can neither be distilled nor manipulated without explosions ranging from rapid decomposition to violent detonation. The hydrocarbon should be stored in the mixture with catalyst used to prepare it, and distilled out as required [1]. The dangerously explosive gel is a peroxidic species not formed in absence of air, when some 1,2-di(3-buten-1-ynyl)cyclobutane is produced by polymerisation [2]. The dienyne reacts readily with atmospheric oxygen, forming an explosively unstable polymeric peroxide. Equipment used with it should be rinsed with a dilute solution of a polymerisation inhibitor to prevent formation of unstable residual films. Adequate shielding of operations is essential [3].

See other ALKYNES, DIENES, POLYPEROXIDES

2285. 1,5-Hexadiyne

[628-16-0] **C_6H_6**



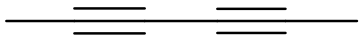
Grignard, 1935, Vol. 3, 181

At the end of distillation at 86°C/1 bar, the last drop ignited. It explodes if heated to 100—120°C, and the copper(I) salt also ignites.

See other ALKYNES

2286. 2,4-Hexadiyne

[2809-69-0] **C_6H_6**



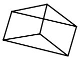
1. Bohlman, F., *Chem. Ber.*, 1951, **84**, 785—794
2. Armitage, J. B., *J. Chem. Soc.*, 1951, 45

Filtration through alumina, which prevents explosion on subsequent distillation at 55°C/13 μbar [1], or at ambient pressure [2], presumably removes peroxidic impurities.

See other ALKYNES

2287. Prismane

[650-42-0] **C_6H_6**



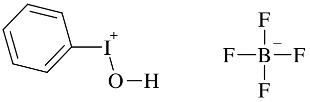
Katz, T. J. *et al., J. Amer. Chem. Soc.*, 1973, **95**, 2739

This tetracyclic isomer of benzene is an explosive liquid.

See other STRAINED-RING COMPOUNDS

2288. Iodosylbenzene tetrafluoroborate

[120312-56-3] **$C_6H_6BF_4IO$**



van Look G., *Chem. Eng. News*, 1989 **67**(30), 2

A compound with tetrafluoroboric acid, previously claimed to be a useful safe oxidant, proved not to be on preparation at 0.5 molar scale. It exploded spontaneously while drying in vacuo at room temperature. *Chem. Abs.* (**112** 98095p) identifies it with this title compound, which was claimed to be too unstable to explode by the original users. It seems more likely that the explosive was the “anhydride”, oxybisphenyliodonium tetrafluoroborate. Several related compounds have also proved to be explosive.

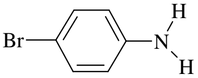
See Oxybisphenyliodonium bistetrafluoroborate

See also Iodosylbenzene

See other IODINE COMPOUNDS

2289. 4-Bromoaniline

[106-40-1] **C_6H_6BrN**



HCS 1980, 220

Energy of decomposition (in range 220—270°C) measured as 0.428 kJ/g.

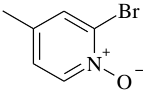
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Nitrous acid

See other HALOANILINES

2290. 2-Bromo-4-methylpyridine *N*-oxide

[17117-12-3] **C_6H_6BrNO**



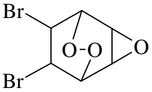
Preparative hazard

See 3-Chloroperoxybenzoic acid: 2-Bromo-4-methylpyridine

See other N-OXIDES

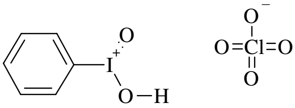
2291. 2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane

[56411-66-6] **$C_6H_6Br_2O_3$**



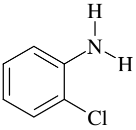
Sasaoka, M. *et al., J. Org. Chem.*, 1979, **44**, 373 (footnote 10)
It explodes on heating.
See other CYCLIC PEROXIDES, 1,2-EPOXIDES

2292. (Hydroxy)(oxo)(phenyl)-λ^3-iodanium perchlorate (Iodylbenzene perchlorate)
[101672-14-4] **$C_6H_6ClIO_6$**



Masson, I., *J. Chem. Soc.*, 1935, 1674
A small sample exploded very violently while still damp.
See other IODINE COMPOUNDS, NON-METAL PERCHLORATES

2293. 2-Chloroaniline
[95-51-2] **C_6H_6ClN**

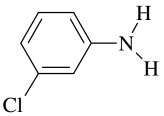


HCS 1980, 295

Heat of decomposition was determined as 0.41 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

Nitrous acid
See other HALOANILINES

2294. 3-Chloroaniline
[108-42-9] **C_6H_6ClN**

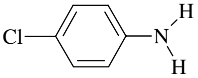


Heat of decomposition was determined as zero.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

Nitrous acid
See other HALOANILINES

2295. 4-Chloroaniline

[106-47-8] **C_6H_6ClN**



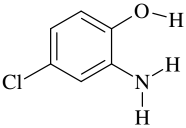
HCS 1980, 294

Energy of exothermic decomposition in range 210—400°C was measured as 0.63kJ/g by DSC, and T_{ait24} was determined as 200°C by adiabatic Dewar tests, with an apparent energy of activation of 124 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Nitrous acid
See DIAZONIUM SULFIDES AND DERIVATIVES (references 8. 9)
See other HALOANILINES

2296. 4-Chloro-2-aminophenol

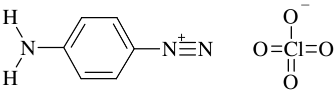
[95-85-2] **C_6H_6ClNO**



T_{ait24} was determined as 110°C by adiabatic Dewar tests, with an apparent energy of activation of 140 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other HALOANILINES

2297. 4-Aminobenzenediazonium perchlorate

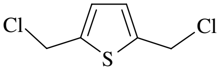
[ ] **$C_6H_6ClN_3O_4$**



Hofmann, K. A. *et al., Ber.*, 1910, **43**, 2624
Extremely explosive.
See other DIAZONIUM PERCHLORATES

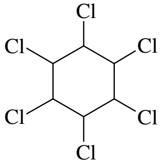
2298. 2,5-Bis(chloromethyl)thiophene

[28569-48-4] **$C_6H_6Cl_2S$**



Griffing, J. M. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 3417
It polymerises at ambient temperature and must therefore be stored cold.
See other 2-HALOMETHYL-FURANS OR -THIOPHENES

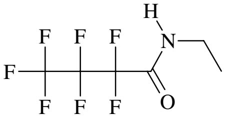
2299. 1,2,3,4,5,6-Hexachlorocyclohexane
[608-73-1] **$C_6H_6Cl_6$**



Dimethylformamide

'DMF Brochure', Billingham, ICI, 1965
There is a potentially dangerous reaction of hexachlorocyclohexane with DMF in presence of iron. The same occurs with carbon tetrachloride, but not with dichloromethane or 1,2-dichloroethane under the same conditions.
See N,N-Dimethylacetamide: Halogenated compounds
See other CATALYTIC IMPURITY INCIDENTS
See related HALOALKANES

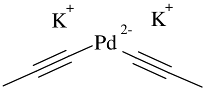
2300. *N*-Ethylheptafluorobutyramide
[70473-76-6] **$C_6H_6F_7NO$**



Lithium tetrahydroaluminate

See Lithium tetrahydroaluminate: Fluoroamides

2301. Potassium bis(propynyl)palladate
[ ] **$C_6H_6K_2Pd$**

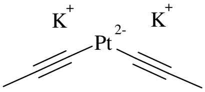


Air, or Water

Immediately pyrophoric in air, and explosive decomposition with aqueous reagents. The sodium salt is similar.
See entry COMPLEX ACETYLIDES

2302. Potassium bis(propynyl)platinate

[ ] **$C_6H_6K_2Pt$**



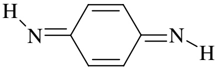
Air, or Water

Pyrophoric in air, explosive decomposition with water, and the sodium salt is similar.

See entry COMPLEX ACETYLIDES

2303. 1,4-Benzoquinone diimine (1,4-Diimido-2,5-cyclohexadiene)

[4377-73-5] **$C_6H_6N_2$**



Acids

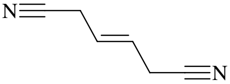
Willstätter, R. *et al., Ber.*, 1906, **37**, 4607

The unstable solid decomposes explosively in contact with conc. hydrochloric acid or sulfuric acid.

See related DIENES

2304. 1,4-Dicyano-2-butene

[1119-69-3] **$C_6H_6N_2$**



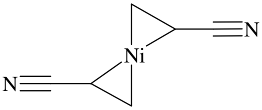
MCA Case History No. 1747

Overheating in a vacuum evaporator initiated accelerating polymerisation-decomposition of (endothermic) dicyanobutene, and the rapid gas evolution eventually caused pressure-failure of the process equipment.

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, GAS EVOLUTION INCIDENTS, POLYMERISATION INCIDENTS

2305. Bis(acrylonitrile)nickel(0)

[12266-58-9] **$C_6H_6N_2Ni$**



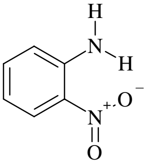
Schrauzer, G. N., *J. Amer. Chem. Soc.*, 1959, **81**, 5310

Pyrophoric in air.

See other CYANO COMPOUNDS, PYROPHORIC MATERIALS

2306. 2-Nitroaniline

[88-74-4] **$C_6H_6N_2O_2$**



Energy of decomposition (in range 280—380°C) measured as 1.81 kJ/g by DSC, and T_{ait24} was determined as 223°C by adiabatic Dewar tests, with an apparent energy of activation of 171 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Hexanitroethane

See Hexanitroethane: Organic compounds

Magnesium, Nitric acid

See Nitric acid: Magnesium, 2-Nitroaniline

Nitrous acid

Preparative hazard

1. Duck, M. W. *et al., Plant/Oper. Progr.*, 1982, **1**, 19—26
2. Willey R. J. *et al., Process Safety Progress*, 2001, **20**(2), 123

Exothermic decomposition of 2-nitroaniline in chemical processes was studied by DSC and ARC techniques. The stability in reaction mixtures was markedly less than for the pure, isolated compound [1]. Later calorimetric study of pyrolysis of 2-nitroaniline in presence of ammonium chloride showed apparent activation energy greater than 200 kJ/mol but reaction enthalpy above 2.1 kJ/g. Maximum rate of pressure rise was 200 bar/min and temperature 400°C/min [2].

See 2-Chloronitrobenzene: Ammonia

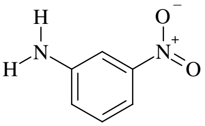
Sulfuric acid

See Sulfuric acid: Nitroaryl bases

See other NITROARYL COMPOUNDS

2307. 3-Nitroaniline

[99-09-2] **$C_6H_6N_2O_2$**



Hakl, J. *et al., Runaway Reactions*, 1981, Paper 3/L, 4, 10

Energy of decomposition (in range 280—380°C) measured as 1.882 kJ/g by DSC, and T_{ait24} was determined as 213°C by adiabatic Dewar tests, with an apparent energy of activation of 149 kJ/mol.

Initial exothermic decomposition occurs at 247°C.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Ethylene oxide

See Ethylene oxide: 3-Nitroaniline

Nitric acid, Sulfuric acid

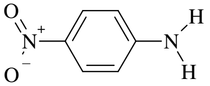
Vanderah, D. J., *J. Energ. Mater.*, 1990, *58*(5), 378

Nitration to 2,3,4,6-tetranitroaniline proved unsafe in mixed acid at 30—50°C. Efficient and safe nitration at 20—30°C was obtained by dissolving the substrate in sulfuric acid, then adding mixed acid (made with oleum) thereto.

See other NITRATION INCIDENTS, NITROARYL COMPOUNDS

2308. 4-Nitroaniline

[100-01-6] **$C_6H_6N_2O_2$**



HCS 1980, 680

Energy of decomposition (in range 280—380°C) measured as 1.882 kJ/g by DSC, and T_{ait24} was determined as 217°C by adiabatic Dewar tests, with an apparent energy of activation of 160 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (REFERENCE 2)

Nitrous acid

Sodium hydroxide

See Sodium 4-nitrophenoxide

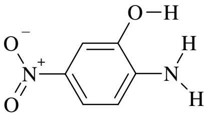
Sulfuric acid

See Sulfuric acid: Nitroaryl bases

See other NITROARYL COMPOUNDS

2309. 2-Amino-5-nitrophenol

[121-88-0] **$C_6H_6N_2O_3$**



Nitrous acid

Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 53

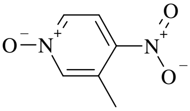
An explosion in a poorly maintained and infrequently cleaned rubber lined vessel used for diazotisation of 2-amino-5-nitrophenol was attributed to decomposition of traces of a diazonium derivative (possibly 4-nitrobenzenediazonium-2-oxide) which had accumulated and dried out on the underside of the lid.

See ARENEDIAZONIUM OXIDES

See other NITROARYL COMPOUNDS

2310. 3-Methyl-4-nitropyridine *N*-oxide

[1074-98-2] **$C_6H_6N_2O_3$**



Preparative hazard

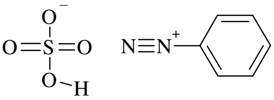
1. Ross, W. C. J., *J. Chem. Soc. C*, 1966, 1816
2. Kuilen, A. v. d. *et al., Chem. Eng. News*, 1989, **67**(5), 2
3. Baumgarten, H. E., *J. Amer. Chem. Soc.*, 1957, **79**, 3145

An explosion occurred during attempted preparation of the title compound following a published procedure. This involved conversion of 3-methylpyridine to the *N*-oxide by treatment with hydrogen peroxide in glacial acetic acid, vacuum evaporation of the volatiles, and then addition of sulfuric and nitric acids, followed by slight warming to effect nitration [1]. Soon after warming the final mixture, a vigorous reaction set in, followed by an explosion. This was attributed to the presence of residual conc. peracetic acid in the *N*-oxide, and its subsequent detonation by the nitration exotherm [2]. An alternative procedure for preparing *N*-oxides precludes formation of peracetic acid [3].

See other NITRATION INCIDENTS, N-OXIDES

2311. Benzenediazonium hydrogen sulfate

[36211-73-1] **$C_6H_6N_2O_4S$**



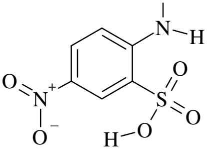
Sorbe, 1968, 122

The salt explodes at about 100°C, but not on impact.

See other DIAZONIUM SULFATES

2312. 4-Nitroaniline-2-sulfonic acid

[96-75-3] **$C_6H_6N_2O_5S$**

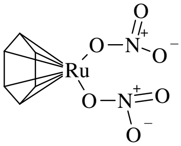


See Sulfuric acid: Nitroaryl bases

See other NITROARYL COMPOUNDS, ORGANIC ACIDS

2313. η⁶-Benzeneruthenium(II) dinitrate

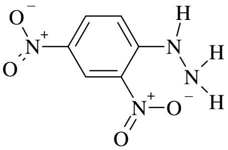
[ ] **$C_6H_6N_2O_6Ru$**



Bennett, M. A. *et al., Organometallics*, 1992, **11**(9), 3069
This compound is a shock sensitive explosive.
See other ORGANOMETALLIC NITRATES

2314. 2,4-Dinitrophenylhydrazine

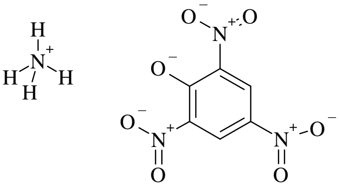
[119-26-6] **$C_6H_6N_4O_4$**



This spot-test reagent is now supplied water-wet since it has been found to be detonable and legally classifiable as an explosive. The editor has not heard of any problems in use.
See other POLYNITROARYL COMPOUNDS

2315. Ammonium picrate

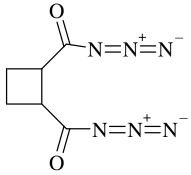
[131-74-8] **$C_6H_6N_4O_7$**



Unpublished data.
A small sample, isolated incidentally during decomposition of a picrate with ammonia, exploded during analytical combustion. The presence of traces of metallic picrates (arising from metal contact) increases heat sensitivity. The salt may also explode on impact.
See other PICRATES, POLYNITROARYL COMPOUNDS

2316. *cis*-1,2-Bis(azidocarbonyl)cyclobutane (Cyclobutane-1,2-dicarboxylic acid diazide)

[ ] $C_6H_6N_6O_2$



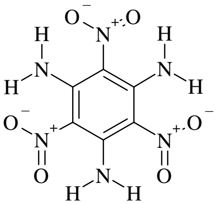
Landgrebe, J. A., *Chem. Eng. News*, 1981, **59**(17), 47

Explosion during preparation is reported for this and its cyclopropane analogue.

See other ACYL AZIDES

2317. 1,3,5-Triaminotrinitrobenzene

[3058-38-6] $C_6H_6N_6O_6$



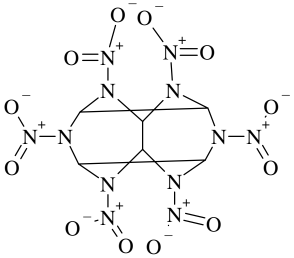
Hydroxylaminium perchlorate

See Hydroxylaminium perchlorate: 1,3,5-Triaminotrinitrobenzene

See other POLYNITROARYL COMPOUNDS

2318. Hexanitrohexaazaisowurtzitane (Octahydro-1,3,4,7,8,10-hexanitro-5,2,6-(iminomethenimino-1*H*-imidazo[4,5-*b*]pyrazine))

[135285-90-4] $C_6H_6N_{12}O_{12}$



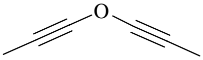
Borman, S., *Chem. Eng. News*, 1994, **72**(3), 18

This nitramine is claimed to be the most energetic molecular explosive known to man (which the editor doubts).

See other N—NITRO COMPOUNDS

2319. Di(1-propynyl) ether (Propargyl ether)

[ ] **C_6H_6O**



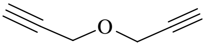
Brandsma, L. *et al., Rec. Trav. Chim.*, 1962, **81**, 510

It is unstable, exploding at ambient temperature.

See other ACETYLENIC COMPOUNDS

2320. Di(2-propynyl) ether (Dipropargyl ether)

[6921-27-3] **C_6H_6O**



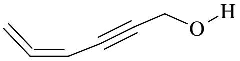
Guide for Safety, 1972, 302

Distillation of the ether in a 230 l still led to an explosion, attributable to peroxidation.

See other ACETYLENIC COMPOUNDS, PEROXIDISABLE COMPOUNDS

2321. 4,5-Hexadien-2-yn-1-ol

[2749-79-3] **C_6H_6O**



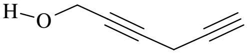
Brandsma, 1971, 8, 54

Dilution with white mineral oil before distillation is recommended to prevent explosion of the concentrated distillation residue.

See other ACETYLENIC COMPOUNDS, DIENES, PEROXIDISABLE COMPOUNDS

2322. 2,5-Hexadiyn-1-ol

[28255-99-4] **C_6H_6O**



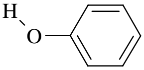
Houben-Weyl, 1977, Vol. 5.2a, 480

The residue after vacuum distillation (at 59—62°C/0.7 mbar) may explode on strong heating or on admission of air, unless mineral oil diluent is present.

See other ACETYLENIC COMPOUNDS, PEROXIDISABLE COMPOUNDS

2323. Phenol (Hydroxybenzene)

[108-95-2] **C_6H_6O**



(*MCA SD-4*, 1964); *NSC 405*, 1978; *FPA H82*, 1979; *HCS 1980*, 725; *RSC Lab. Hazards Data Sheet No. 42*, 1985

Aluminium chloride, Nitrobenzene
See Aluminium chloride: Nitrobenzene, etc.

Aluminium chloride—nitromethane complex, Carbon monoxide
See Aluminium chloride—nitromethane: Carbon monoxide, etc.

Chlorodiphenylmethane
See Chlorodiphenylmethane

Formaldehyde
See Formaldehyde: Phenol

Other reactants
Yoshida, 1980, 295
MRH values calculated for 15 combinations, largely with oxidants, are given.

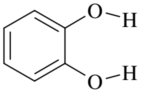
Peroxodisulfuric acid
See Peroxodisulfuric acid: Organic liquids

Peroxomonosulfuric acid
See Peroxomonosulfuric acid: Aromatic compounds

Sodium nitrate, Trifluoroacetic acid
See Sodium nitrate: Phenol, etc.

Sodium nitrite
See Sodium nitrite: Phenol

2324. 1,2-Benzenediol (Pyrocatechol)
[120-80-9] **$C_6H_6O_2$**

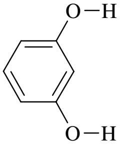


HCS 1980, 285

Nitric acid MRH 5.73/74
See Nitric acid: Pyrocatechol

Other reactants
Yoshida, 1980, 89
MRH values calculated for 13 combinations with oxidants are given.

2325. 1,3-Benzenediol (Resorcinol)
[108-46-3] **$C_6H_6O_2$**

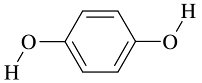


Nitric acid

See Nitric acid: Resorcinol

2326. 1,4-Benzenediol (Hydroquinone)

[123-31-9] **$C_6H_6O_2$**



HCS 1980, 554

Other reactants

Yoshida, 1980, 287

MRH values calculated for 13 combinations, largely with oxidants, are given.

Oxygen

See Oxygen (Gas): 1,4-Benzenediol

Sodium hydroxide MRH 1.09/tr.

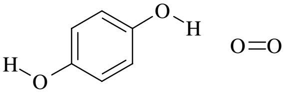
491M, 1975, 385

Accidental mixing of the hot crude hydroquinone with conc. sodium hydroxide solution led to extensive exothermic decomposition.

See other REDUCANTS

2327. 1,4-Benzenediol—oxygen complex (Hydroquinone—oxygen clathrate)

[20471-57-2] **$C_6H_6O_2.O_2$**

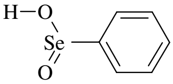


Preparative hazard

See Oxygen: 1,4-Benzenediol

2328. Benzeneseleninic acid

[6996-92-5] **$C_6H_6O_2Se$**



Hydrazine derivatives

Back, T. G. *et al., J. Org,. Chem.*, 1981, **46**, 1568

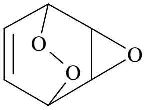
The acid or its anhydride react very vigorously with hydrazine derivatives in absence of solvent. A solid mixture of the acid with benzohydrazide reacted violently after an induction period of several minutes.

See other INDUCTION PERIOD INCIDENTS, ORGANIC ACIDS

Preparative hazard

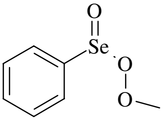
See Hydrogen peroxide: Diphenyl diselenide

2329. *endo*-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene (Oxepin-3,6-endoperoxide)
[39597-90-5] **$C_6H_6O_3$**



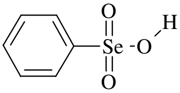
Foster, C. H. *et al., J. Org. Chem.*, 1975, **40**, 3744
Evaporation of (peroxide-contacted) solvent ether from 9.8 g of crude peroxide led to an explosion. Subsequent preparations were effected on a smaller scale.
See other CYCLIC PEROXIDES, 1,2-EPOXIDES

2330. Benzeneperoxyseleninic acid
[62865-92-6] **$C_6H_6O_3Se$**



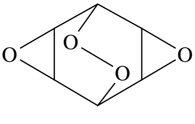
Syper, L. *et al., Tetrahedron*, 1987, **43**, 207—213
It explodes at the m.p., 52°C.
See other PEROXYACIDS

2331. Benzeneselenonic acid
[39254-48-3] **$C_6H_6O_3Se$**



Stöcker, M. *et al., Ber.*, 1906, **39**, 2917
It explodes feebly at 180°C but the silver salt is more explosive.
See other ORGANIC ACIDS

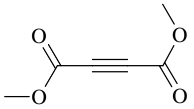
2332. 2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane
[56411-67-7] **$C_6H_6O_4$**



Sasaoka, M. *et al., J. Org. Chem.*, 1979, **44**, 373 (footnote 10)
It explodes when heated.
See other CYCLIC PEROXIDES, 1,2-EPOXIDES

2333. Dimethyl acetylenedicarboxylate (Dimethyl 2-butynedioate)

[762-42-5] **$C_6H_6O_4$**



Energy of decomposition (in range 150—430°C) measured as 1.224 kJ/g by DSC, and T_{ait24} was determined as 86°C by adiabatic Dewar tests, with an apparent energy of activation of 91 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

1-Methylsilacyclopenta-2,4-diene

See 1-Methylsilacyclopenta-2,4-diene: Dienophiles

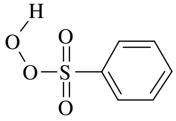
Octakis(trifluorophosphine)dirhodium

See Octakis(trifluorophosphine)dirhodium: Acetylenic esters

See other ACETYLENIC COMPOUNDS

2334. Benzeneperoxysulfonic acid

[ ] **$C_6H_6O_4S$**



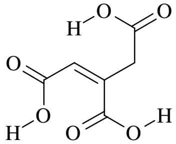
Preparative hazard

See Hydrogen peroxide: Benzenesulfonic anhydride

See other PEROXYACIDS

2335. *E*-Propene-1,2,3-tricarboxylic acid (Aconitic acid)

[4023-65-8] **$C_6H_6O_6$**



Hydrogen peroxide

See Hydrogen peroxide: Aconitic acid

See other ORGANIC ACIDS

2336. Benzene triozonide (Ozobenzene)

[71369-69-2] **$C_6H_6O_9$**

[1790]

1. Harries, C. *et al., Ber.*, 1904, **37**, 3431

2. *DOC 5*, 1982, Vol. 4, 4471

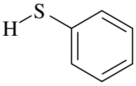
The product of ozonising benzene exhaustively is extremely explosive at the slightest touch [1]. The structure is not well defined as previously thought, but is probably polymeric [2].

See Ozone: Aromatic compounds

See other OZONIDES

2337. Benzenethiol (Thiophenol)

[108-98-5] **C_6H_6S**



HCS 1980, 189

Preparative hazard

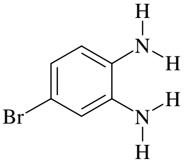
1. Leuckart, R., *J. Prakt. Chem.*, 1890, **41**, 179
2. Graesser, R., private comm., 1968

During preparation of thiophenol by addition of a cold solution of potassium *O*-methyldithiocarbonate to a cold solution of benzenediazonium chloride, a violent explosion accompanied by an orange flash occurred [1]. This was attributed to the formation and decomposition of bis(benzenediazo) disulfide. A preparation in which the diazonium solution was added to the 'xanthate' solution proceeded smoothly [2].

See also DIAZONIUM SULFIDES AND DERIVATIVES

2338. 4-Bromo-1,2-diaminobenzene

[1575-37-7] **$C_6H_7BrN_2$**

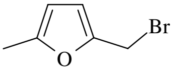


T_{ait24} was determined as the rather low value of 70°C by adiabatic Dewar tests, with an apparent energy of activation of 133 kJ/mol.

See related HALOANILINES

2339. 2-Bromomethyl-5-methylfuran

[57846-03-4] **C_6H_7BrO**



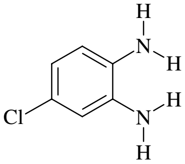
Dunlop, 1953, 261

It distils with violent decomposition at 70°C/33 mbar.

See other 2-HALOMETHYL-FURANS OR -THIOPHENES

2340. 4-Chloro-1,2-benzenediamine

[95-83-0] **$C_6H_7ClN_2$**

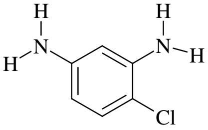


Energy of decomposition (in range 160—260°C) measured as 0.78 kJ/g by DSC, and T_{ait24} was determined as 100°C by adiabatic Dewar tests, with an apparent energy of activation of 140 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See related HALOANILINES

2341. 4-Chloro-1,3-benzenediamine

[5131-60-2] **$C_6H_7ClN_2$**

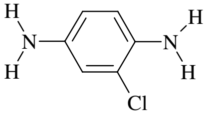


Energy of decomposition (in range 200—250°C) measured as 1.13 kJ/g by DSC, and T_{ait24} was determined as 1006°C by adiabatic Dewar tests, with an apparent energy of activation of 121 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See related HALOANILINES

2342. 2-Chloro-1,4-benzenediamine

[615-66-7] **$C_6H_7ClN_2$**



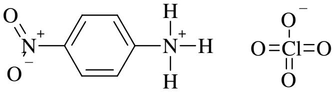
Frankenberg, P. E., *Chem. Eng. News*, 1982, **60**(3), 97

Violently explosive decomposition at the start of distillation at 165°C/33 mbar of a 2 kg sample was attributed to autocatalytic decomposition which can occur at 125°C in small samples. Increased lability of the 2-chloro substituent when hydrochloride formation has occurred is postulated as a possible cause. Caution on heating any halogenated amine is advised.

See 2-Chloroethylamine
See other HALOANILINES

2343. 4-Nitroanilinium perchlorate

[15873-50-4] **$C_6H_7ClN_2O_6$**



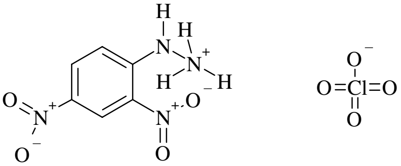
Jain, S. R. *et al., Combust. Flame*, 1979, **35**, 289—295

Of a series of substituted anilinium perchlorate salts, that of 4-nitroaniline showed the lowest thermal stability (DTA peak temperature 201°C) and highest shock-sensitivity.

See other NITROARYL COMPOUNDS, PERCHLORATE SALTS OF NITROGENOUS BASES

2344. 2,4-Dinitrophenylhydrazinium perchlorate

[104503-71-1] **$C_6H_7ClN_4O_8$**



Anon., *Angew. Chem. (Nachr.)*, 1967, **15**, 78

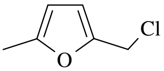
Although solutions of the perchlorate are stable as prepared, explosive decomposition may occur during concentration by heated evaporation.

See also HYDRAZINIUM SALTS

See other PERCHLORATE SALTS OF NITROGENOUS BASES, POLYNITROARYL COMPOUNDS

2345. 2-Chloromethyl-5-methylfuran

[52157-57-0] **C_6H_7ClO**



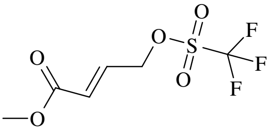
Dunlop, 1953, 261

It is even more unstable than its lower homologue, 2-chloromethylfuran.

See other 2-HALOMETHYL-FURANS OR -THIOPHENES

2346. 3-Methoxycarbonylpropen-2-yl trifluoromethanesulfonate
(Methyl 4-(trifluorosulfonyloxy)but-2-enoate)

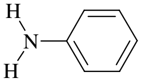
[62861-57-8] **$C_6H_7F_3O_5S$**



See entry ALLYL TRIFLUOROMETHANESULFONATES

2347. Aniline (Benzeneamine)

[62-53-3] **C_6H_7N**



(*MCA SD-17*, 1963); *NSC 409*, 1979; *FPA H80*, 1979; *HCS 1980*, 156; *RSC Lab. Hazard Data Sheet No. 23,* 1984

Anilinium chloride

Anon., *Chem. Met. Eng.*, 1922, **27**, 1044

Heating a mixture of the components in an autoclave at 240—260°C/7.6 bar to produce diphenylamine led to a violent explosion, following a sudden increase in pressure to 17 bar. The equipment and process had been used previously and uneventfully.

Benzenediazonium-2-carboxylate

See Benzenediazonium-2-carboxylate
    Benzenediazonium-2-carboxylate: Aniline, etc.

Boron trichloride

See Boron trichloride: Aniline

1-Chloro-2,3-epoxypropane

See 1-Chloro-2,3-epoxypropane: Aniline

Dibenzoyl peroxide

See Dibenzoyl peroxide: Aniline

Nitromethane MRH 5.69/99+

See Nitromethane: Acids, etc.

Nitrous acid

See DIAZONIUM SALTS

Other reactants

Yoshida, 1980, 22

MRH values calculated for 20 combinations with oxidants are given.

Oxidants MRH values show % of oxidant

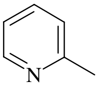
See Diisopropyl peroxydicarbonate: Amines, etc.
    'Fluorine nitrate': Organic materials
    Fluorine: Nitrogenous bases
    Hydrogen peroxide: Organic compounds (reference 2) MRH 6.44/83
    Nitric acid: Aromatic amines MRH 5.98/81
    Nitrosyl perchlorate: Organic materials
    Ozone: Aromatic compounds MRH 11.5/72
    Perchloric acid: Aniline, etc. MRH 6.65/82
    Perchloryl fluoride: Nitrogenous bases
    Peroxodisulfuric acid: Organic liquids

Peroxomonosulfuric acid: Aromatics
Peroxyformic acid: Organic materials
Sodium peroxide: Organic liquids, etc. MRH 2.76/93
See N-HALOIMIDES: ALCOHOLS, AMINES

Tetranitromethane
See Tetranitromethane: Amines

Trichloronitromethane MRH 2.38/64
See Trichloronitromethane: Aniline

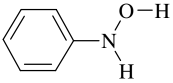
2348. 2-Methylpyridine (2-Picoline)
[109-06-8] **C_6H_7N**



HCS 1980, 754

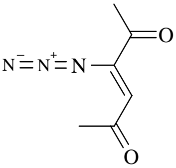
Hydrogen peroxide, Iron(II) sulfate, Sulfuric acid
See Hydrogen peroxide: Iron(II) sulfate, etc.
See other ORGANIC BASES

2349a. *N*-Phenylhydroxylamine (*N*-Hydroxybenzeneamine)
[100-65-2] **C_6H_7NO**



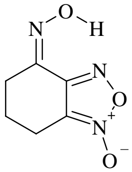
Preparative hazard
See Phenylhydroxylaminium chloride
See Zinc: Nitrobenzene
See other N—O COMPOUNDS
See other ORGANIC BASES

2349b. 3-Azido-3-hexene-2,5-dione
[116139-27-6] **$C_6H_7N_3O_2$**



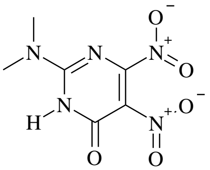
Sauers, R. R. *et al., Phosphorus, Sulfur, Silicon and related Elements*, 2003, **178**(10), 2169
The E- isomer decomposed explosively on standing [1]. There is no reason to suppose the other isomer would be more stable.
See other 2-AZIDOCARBONYL COMPOUNDS

2350. 4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide
[ ] **$C_6H_7N_3O_3$**



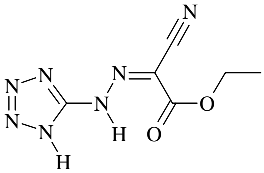
Preparative hazard
See Sulfinyl chloride: 1,2,3-Cyclohexanetrione trioxime, etc.
See other FURAZAN N-OXIDES, OXIMES

2351. 2-Dimethylamino-5,6-dinitro-pyrimidinone
[ ] **$C_6H_7N_5O_5$**



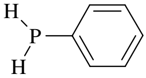
Tennant, G. *et al., J. Chem. Soc., Chem. Comm.*, 1982, 61
It decomposed violently on melting at 190°C.
See related POLYNITROARYL COMPOUNDS

2352. Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate
[61033-15-6] **$C_6H_7N_7O_2$**



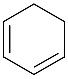
Preparative hazard
See 5-Aminotetrazole (reference 3)
See other CYANO COMPOUNDS, TETRAZOLES

2353. Phenylphosphine
[638-21-1] **C_6H_7P**



Haszeldine, R. N. *et al., J. Fluorine Chem.*, 1977, **10**, 38
It is pyrophoric in air.
See related ALKYLPHOSPHINES

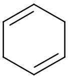
†2354. 1,3-Cyclohexadiene
[592-57-4] **C_6H_8**



1. Bodendorf, K., *Arch. Pharm.*, 1933, **271**, 11
2. Hock, H. *et al., Chem. Ber.*, 1951, **84**, 349

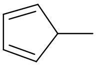
Cyclohexadiene autoxidises slowly in air, but the residual (largely polymeric) peroxide explodes very violently on ignition [1]. The monomeric peroxide has also been isolated [2].
See Propene
See other DIENES, POLYPEROXIDES

†2355. 1,4-Cyclohexadiene
[628-41-1] **C_6H_8**



See Propene
See other DIENES

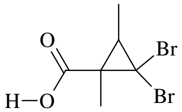
2356. Methylcyclopentadiene
[26519-91-5] **C_6H_8**



Bis(pentafluorophenyl)ytterbium
See Bis(pentafluorophenyl)ytterbium: Methylcyclopentadiene
See other DIENES

2357. 2,2-Dibromo-1,3-dimethylcyclopropanoic acid

[72957-64-3] **$C_6H_8Br_2O_2$**

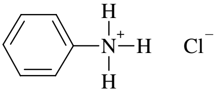


tert-Butylamine

Baird, M. S. *et al., J. Chem. Soc., Perkin Trans. 1*, 1979, 2324
Interaction is highly exothermic.
See other ORGANIC ACIDS

2358. Anilinium chloride

[142-04-1] **C_6H_8ClN**

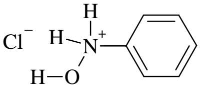


HCS 1980, 157

Aniline
See Aniline: Anilinium chloride

2359. Phenylhydroxylaminium chloride

[22755-09-5] **C_6H_8ClNO**

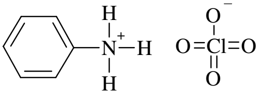


MCA Guide, 1972, 299

A brown glass bottle containing 700 g of the salt exploded forcefully after shelf storage for 2 weeks.
See HYDROXYLAMINIUM SALTS
See other N—O COMPOUNDS

2360. Anilinium perchlorate

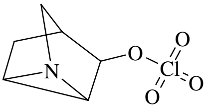
[14796-11-3] **$C_6H_8ClNO_4$**



Metal oxides
Rao, M. V. *et al., Combust. Flame*, 1980, **39**, 63—68

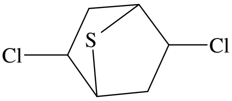
The effect of metal oxides in sensitising the thermal decomposition and explosion of the salt is in the order: manganese dioxide > copper oxide > nickel oxide.
See other AMINIUM PERCHLORATES, PERCHLORATE SALTS OF NITROGENOUS BASES

2361. 2-Azatricyclo[2.2.1.0^{2,6}]hept-7-yl perchlorate
[98566-27-9] **$C_6H_8ClNO_4$**



Durrant, M. L. *et al., J. Chem. Soc., Chem. Comm.*, 1985, 1879
A crystalline sample exploded without warning in the freezer compartment of a refrigerator.
See related ALKYL PERCHLORATES, PERCHLORATE SALTS OF NITROGENOUS BASES, STRAINED-RING COMPOUNDS

2362. *endo*-2,5-Dichloro-7-thiabicylo[2.2.1]heptane
[6522-40-3] **$C_6H_8Cl_2S$**

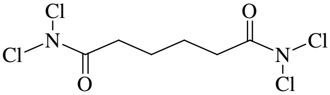


Dimethylformamide, Sodium tetrahydroborate

1. Corey, E. J. *et al., J. Org. Chem.*, 1969, **34**, 1234 (footnote 5)
2. Paquette, L. A., private comm., 1975
3. Brown, H. C. *et al., J. Org. Chem.*, 1962, **27**, 1928—1929

To effect reduction to the parent heterocycle, a solution of the dichloro compound in DMF was being added to a hot solution of sodium tetrahydroborate in the same solvent, when a violent explosion occurred [1,2]. This may have arisen either from interaction of the dichloro compound with the solvent, or from the known instability of hot solutions of the tetrahydroborate in DMF. Use of aqueous diglyme as an alternative solvent [3] would only be applicable to this and other hydrolytically stable halides [2].
See Dimethylformamide: Halocarbons
Sodium tetrahydroborate: Dimethylformamide
See HALOCARBONS

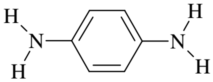
2363. *N,N,N‘,N’*-Tetrachloroadipamide
[ ] **$C_6H_8Cl_4N_2O_2$**



Water
See DICHLORAMINE
See other N-HALOGEN COMPOUNDS

2364. 1,4-Diaminobenzene (*p*-Phenylenediamine)

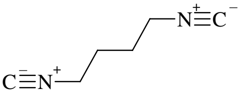
[106-50-3] **$C_6H_8N_2$**



The finely powdered base is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)
See other ORGANIC BASES

2365. 1,4-Diisocyanobutane

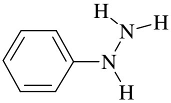
[929-25-9] **$C_6H_8N_2$**



See entry DIISOCYANIDE LIGANDS
See related CYANO COMPOUNDS

2366. Phenylhydrazine

[100-63-0] **$C_6H_8N_2$**



HCS 1980, 735

et al., Exothermic Decomposition, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
Energy of decomposition (in range 280—375°C) measured as 0.662 kJ/g by DSC, and T_{ait24} was determined as 227°C by adiabatic Dewar tests, with an apparent energy of activation of 165 kJ/mol.

Heat of decomposition was determined as 0.65 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

Lead(IV) oxide MRH 0.46/95
See Lead(IV) oxide: Nitrogen compounds

Other reactants
Yoshida, 1980, 294
MRH values calculated for 13 combinations with oxidants are given.

Perchloryl fluoride
See Perchloryl fluoride: Nitrogenous bases

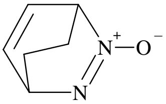
α-Phenylazo hydroperoxide

See α-Phenylazo hydroperoxide: Phenylhydrazine

See other ORGANIC BASES, REDUCANTS

2367. 2,3-Diazabicyclo[2.2.2]octa-2,5-diene *N*-oxide

[37436-17-2] **$C_6H_8N_2O$**



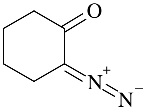
Preparative hazard

See Hydrogen peroxide: 4-Methyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undeca-8-ene-3,5-dione, etc.

See other N-OXIDES

2368. 2-Diazocyclohexanone

[3242-56-6] **$C_6H_8N_2O$**



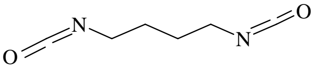
Regitz, M. *et al., Org. Synth.*, 1971, **51**, 86

It may explode on being heated, and a relatively large residue should be left during vacuum distillation to prevent overheating.

See other DIAZO COMPOUNDS

2369. Butane-1,4-diisocyanate

[4538-37-8] **$C_6H_8N_2O_2$**



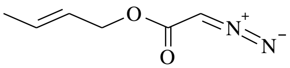
Zlobin, V. A. *et al., Chem. Abs.*, 1987, **107**, 39144

Conditions for the safe preparation of the diisocyanate from adipoyl chloride and sodium azide in acetonitrile—toluene mixtures were established.

See other ORGANIC ISOCYANATES

2370. 2-Buten-1-yl diazoacetate

[14746-03-3] **$C_6H_8N_2O_2$**



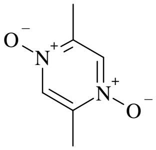
Blankley, C. J. *et al., Org. Synth.*, 1969, **49**, 25

Precautions are necessary during vacuum distillation of this potentially explosive material.

See other DIAZO COMPOUNDS

2371. 2,5-Dimethylpyrazine 1,4-dioxide

[6890-38-6] **$C_6H_8N_2O_2$**



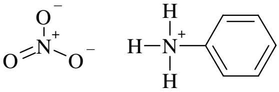
Preparative hazard

See Hydrogen peroxide: Acetic acid, *N*-Heterocycles

See other N-OXIDES

2372. Anilinium nitrate

[542-15-4] **$C_6H_8N_2O_3$**



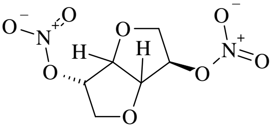
Nitric acid

See Nitric acid: Anilinium nitrate

See other OXOSALTS OF NITROGENOUS BASES

2373. Isosorbide dinitrate (1,4:3,6-Dianhydro-*D*-glucitol dinitrate)

[87-33-2] **$C_6H_8N_2O_8$**



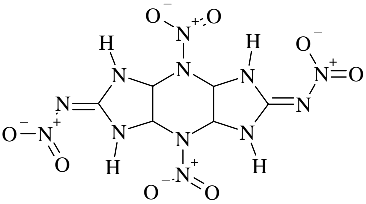
Reddy, G. O. *et al., J. Hazard. Mater.*, 1992, **32**(1), 87

This heart drug is detonable when dry but non-explosive with 30% of water.

See other ALKYL NITRATES

2374. Dodecahydro-4,8-dinitro-2,6-bis(nitroimino)diimidazo[4,5-*b*:4’,5’-*e*]pyrazine

[134927-04-1] **$C_6H_8N_{12}0_8$**



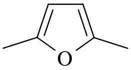
Dagley, I. J. *et al., J. Energ. Mater.*, 1995, **13**(1&2), 35

This nitroguanidine analogue is more sensitive than RDX to friction, but equivalent by the drop-weight impact test.

See other N—NITRO COMPOUNDS

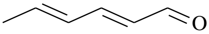
†2375. 2,5-Dimethylfuran

[625-86-5] **C_6H_8O**



2377. 2,4-Hexadienal

[142-83-6] **C_6H_8O**



1-Amino-2-propanol

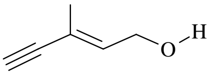
Steele, A. B. *et al., Chem. Engrg.*, 1959, *66*(8), 166

Following a plant incident in which the crude aldehyde had polymerised during distillation, it was found that the presence of 2% of isopropanolamine (a probable impurity) led to an explosive polymerisation reaction. It is conceivable that aldehydic peroxides may also have been involved.

See other PEROXIDISABLE COMPOUNDS, POLYMERISATION INCIDENTS

2378. 3-Methyl-2-penten-4-yn-1-ol

[105-29-3] **C_6H_8O**



1. Lorentz, F., *Loss Prev.*, 1967, **1**, 1—5
2. Fesenko, G. V. *et al., Chem. Abs.*, 1975, **83**, 47605

Temperature control during pressure hydrogenation of *cis*- or *trans*-isomers is essential, since at 155°C violent decomposition to carbon, hydrogen and carbon monoxide with development of over 1 kbar pressure will occur. The material should not be heated above 100°C, particularly if acid or base is present, to avoid exothermic polymerisation [1]. The *cis*-isomer is readily cyclised to 2,3-dimethylfuran, which promotes fire and explosion hazards. These were measured for the *cis*- and *trans*-isomers, and for *trans*-3-methyl-1-penten-4-yn-3-ol [2].

See other GAS EVOLUTION INCIDENTS, HYDROGENATION INCIDENTS, POLYMERISATION INCIDENTS

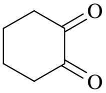
Sodium hydroxide

1. *MCA Case History No. 363*
2. Silver, L., *Chem. Eng. Progr.*, 1967, **63**(8), 43

Presence of traces of sodium hydroxide probably caused formation of the acetylenic sodium salt, which exploded during high-vacuum distillation in a metal still [1]. A laboratory investigation which duplicated the explosion, without revealing the precise cause, was also reported [2].

See other ACETYLENIC COMPOUNDS

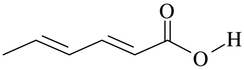
2379a. 1,2-Cyclohexanedione
[765-87-7] **$C_6H_8O_2$**



Preparative hazard

See Nitric acid: 4-Methylcyclohexanone

2379b. 2,4-Hexadienoic acid (Sorbic acid)
[110-44-1] **$C_6H_8O_2$**



The dry finely powdered acid is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

See other ORGANIC ACIDS

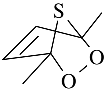
2380. Poly(1,3-cyclohexadiene peroxide)
[ ] **$(C_6H_8O_2)_n$**

[1829]

See 1,3-Cyclohexadiene

See other POLYPEROXIDES

2381. 2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide
[67711-62-0] **$C_6H_8O_2S$**



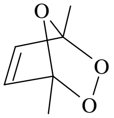
Golnick, K. *et al., Tetrahedron Lett.*, 1984, **25**, 4291—4294

The endoperoxide of 2,5-dimethylthiophene (effectively a thiaozonide) when neat decomposes violently at ambient temperature.

See other CYCLIC PEROXIDES

See related OZONIDES

2382. 1,4-Dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene (2,5-Dimethyl-2,5-dihydrofuran-2,5-endoperoxide)
[45722-89-2] **$C_6H_8O_3$**

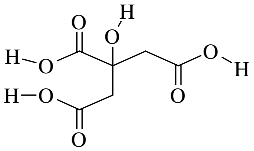


Gollnick, K. *et al., Angew. Chem. (Intern. Ed.)*, 1983, **22**, 726

The solvent-free peroxide always explodes if amounts above 100 mg are handled.

See other CYCLIC PEROXIDES

2383. Citric acid (2-Hydroxypropane-1,2,3-tricarboxylic acid)
[77-92-9] **$C_6H_8O_7$**

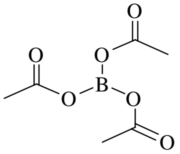


Metal nitrates

See METAL NITRATES: CITRIC ACID

See other ORGANIC ACIDS

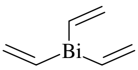
2384. Triacetyl borate
[4887-24-5] **$C_6H_9BO_6$**



Preparative hazard

See Acetic anhydride: Boric acid

2385. Trivinylbismuth
[65313-35-1] **C_6H_9Bi**



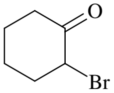
Coates, 1967, Vol. 1, 538

It ignites in air.

See related ALKYLMETALS, TRIALKYLBISMUTHS

2386. 2-Bromocyclohexanone

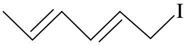
[822-85-5] **C_6H_9BrO**



Energy of decomposition (in range 80—130°C) measured as 0.29 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

2387. 1-Iodohexa-2,4-diene

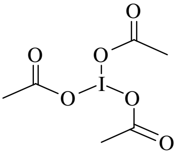
[ ] **C_6H_9I**



Hayashi, T., *et al., J. Chem. Soc., Chem. Comm.*, 1990, (19), 1362
This compound undergoes explosive decomposition when freed of solvent. Homologues are also unstable.
See other DIENES, HALOALKENES, IODINE COMPOUNDS

2388a. Iodine triacetate

[6540-76-7] **$C_6H_9IO_6$**

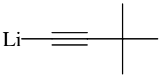


1. Schutzenberger, P., *Compt. rend.*, 1861, **52**, 135
2. Oldham, F. W. H. *et al., J. Chem. Soc.*, 1941, 368

The acetate explodes at 140°C [1], and higher homologues decompose at about 120°C, the violence decreasing with ascent of the homologous series [2].
See other IODINE COMPOUNDS

2388b. Lithium 3,3-dimethylbut-1-ynide (Lithium *t*-butylacetylide)

[37892-71-0] **C_6H_9Li**

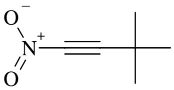


Water
1. Demer, F.R., University of Arizona Lab. Safety Notes, 1992, (summer), 2

An attempt was made to react this with (heavy) water by freezing a solution in toluene in liquid nitrogen, then adding the deuterium oxide, and finally allowing the mix to warm up. After a few minutes there was a violent explosion [2]. This is undoubtedly the result of a runaway produced by overcooling, all components starting below their freezing points, thus unreactive. On freezing the toluene, if not before, the salt will

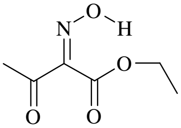
crystallise from it, and probably sink while liquid is present. Deuterium oxide will also find its way beneath any liquid toluene as the mixture rewarms. The reacting components have thus been concentrated at the bottom and will interact exothermically and uncontrollably as the ice melts. Should the lithium salt be lighter than toluene, a similar effect will prevail, though it would then be expected that explosion would occur as the water was added to the butynide crust.
See other METAL ACETYLIDES

2389a. 3,3-Dimethyl-1-nitro-1-butyne (*tert*-Butylnitroacetylene)
[22691-91-4] **$C_6H_9NO_2$**



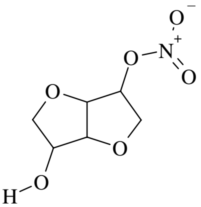
Amines
Jäger, V. *et al., Angew. Chem. (Intern. Ed.)*, 1969, **8**, 273
Reaction with primary, secondary or tertiary amines proceeds explosively with ignition in absence of a solvent.
See other ACETYLENIC COMPOUNDS
See related NITROALKENES

2389b. Ethyl 2-hydroximino-3-oxobutanoate
[5408-04-8] [66508-94-0] *E* [66508-93-8] *Z* **$C_6H_9NO_4$**



Anon. 2004
Rough calorimetry shows this useful intermediate liable to runaway from about 100°C as the crude (almost entirely *Z*) product from nitrosation of acetoacetate. It is greatly destabilised by dimethyl sulfate, mixtures with which run away from between 40 & 50°C.
See other OXIMES

2390. 1,4,3,6-Dianhydroglucitol 2-nitrate (Isosorbide mononitrate)
[16106-20-0] **$C_6H_9NO_6$**



Négyesi, G., *Process Safety Progress*, 1996, **15**(1), 42

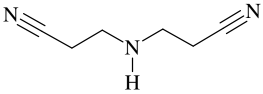
Lead block tests show this to be a feeble explosive, it is not impact sensitive but shows some decomposition on friction.

See Isosorbide dinitrate

See other ALKYL NITRATES

2391. Bis(2-cyanoethyl)amine

[111-94-4] **$C_6H_9N_3$**



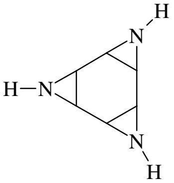
Anon., *BCISC Quart. Safety Summ.*, 1967, **38**, 42

Some 18-month old bottles of 'iminodipropionitrile' exploded, probably owing to slow hydrolysis and release of ammonia.

See other CYANO COMPOUNDS, GAS EVOLUTION INCIDENTS

2392. 3,6,9-Triazatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane (*cis*-Benzene triimine)

[52851-26-0] **$C_6H_9N_3$**



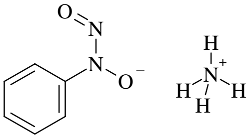
Schwesinger, R. *et al., Angew. Chem. (Intern. Ed.)*, 1973, **12**, 989

It explodes if rapidly heated to 200°C.

See other STRAINED-RING COMPOUNDS

2393. Ammonium *N*-nitrosophenylaminooxide ('Cupferron')

[135-20-6] **$C_6H_9N_3O_2$**



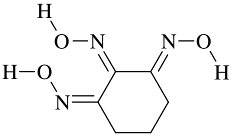
Thorium salts

Pittwell, L. R., *J. R. Inst. Chem.*, 1956, **80**, 173

Solutions of this reagent are destabilised by the presence of thorium ions. If a working temperature of 10—15°C is much exceeded, the risk of decomposition, not slowed by cooling and accelerating to explosion, exists. Titanium and zirconium salts also cause slight destabilisation, but decomposition temperatures are then 35 and 40°C, respectively.

See other NITROSO COMPOUNDS, N—O COMPOUNDS

2394. 1,2,3-Cyclohexanetrione trioxime
[3570-93-2] **$C_6H_9N_3O_3$**

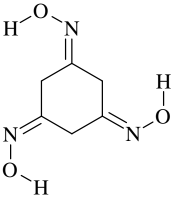


Sulfinyl chloride

See Sulfinyl chloride: 1,2,3-Cyclohexanetrione trioxime, etc.

See other OXIMES

2395. 1,3,5-Cyclohexanetrione trioxime
[621-22-7] **$C_6H_9N_3O_3$**

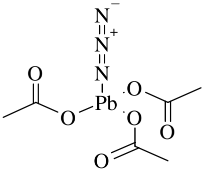


Baeyer, A., *Ber.*, 1886, **19**, 160

The oxime of phloroglucinol explodes rather violently at 155°C.

See other OXIMES

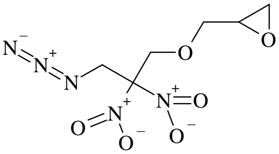
2396. Lead(IV) acetate azide
[ ] **$C_6H_9N_3O_6Pb$**



See Lead(IV) azide

See related METAL AZIDES

2397. 3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide
[76828-34-7] **$C_6H_9N_5O_6$**



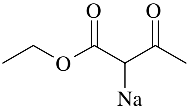
Frankel, M. B. *et al., J. Chem. Eng. Data*, 1981, **26**, 219

The monomeric azide and several precursors are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction or heat.

See other 1,2-EPOXIDES, ORGANIC AZIDES, POLYNITROALKYL COMPOUNDS

2398. Ethyl sodioacetoacetate

[19232-39-4] **$C_6H_9NaO_3$**

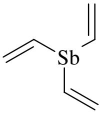


2-Iodo-3,5-dinitrobiphenyl

See 2-Iodo-3,5-dinitrobiphenyl: Ethyl sodioacetoacetate

2399. Trivinylantimony

[5613-68-3] **C_6H_9Sb**



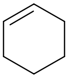
Leleu, *Cahiers*, 1977, (88), 362

It ignites in air.

See related ALKYLMETALS

†2400. Cyclohexene

[110-83-8] **C_6H_{10}**

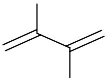


HCS 1980, 346

See other ALKENES

2401. 2,3-Dimethyl-1,3-butadiene

[513-81-5] **C_6H_{10}**



Bodendorf, K., *Arch. Pharm.*, 1933, **271**, 33

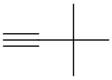
A few mg of the autoxidation residue, a largely polymeric peroxide, exploded violently on ignition.

See other POLYPEROXIDES

Oxygen, Ozone
See Ozone: Dienes, Oxygen

Thiazyl fluoride
See Thiazyl fluoride: Alkylbutadienes
See other DIENES

2402. 3,3-Dimethyl-1-butyne
[917-92-0] **C_6H_{10}**

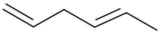


Preparative hazard
See 2,2-Dichloro-3,3-dimethylbutane: Sodium hydroxide
See other ALKYNES

†2403. 1,3-Hexadiene
[592-48-3] **C_6H_{10}**

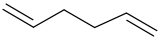
See other DIENES

†2404. 1,4-Hexadiene
[592-45-0] **C_6H_{10}**



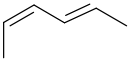
See other DIENES

†2405. 1,5-Hexadiene
[592-42-7] **C_6H_{10}**



See other DIENES

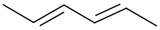
†2406. *cis*-2-*trans*-4-Hexadiene
[5194-50-3] **C_6H_{10}**



See other DIENES

†2407. *trans*-2-*trans*-4-Hexadiene

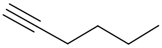
[5194-51-4] **C_6H_{10}**



See other DIENES

†2408. 1-Hexyne

[693-02-7] **C_6H_{10}**



See other ALKYNES

†2409. 3-Hexyne

[928-49-4] **C_6H_{10}**

EtC≡CEt

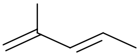
Mercury, Silver perchlorate

See Silver perchlorate: Alkynes, etc.

See other ALKYNES

†2410. 2-Methyl-1,3-pentadiene

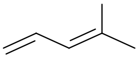
[1118-58-7] **C_6H_{10}**



See other DIENES

†2411. 4-Methyl-1,3-pentadiene

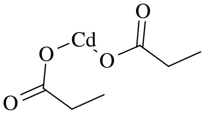
[926-56-7] **C_6H_{10}**



See other DIENES

2412. Cadmium propionate

[16986-83-7] **$C_6H_{10}CdO_4$**

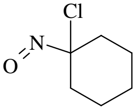


Anon., *Chem. Age*, 1957, **77**, 794

The salt exploded during drying at 60—100°C in an electric oven, presumably because of overheating which caused pyrolysis to 3-pentanone and ignition of its vapour.
See other HEAVY METAL DERIVATIVES

2413. 1-Chloro-1-nitrosocyclohexane

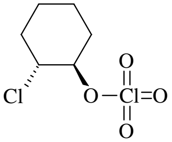
[695-64-7] **$C_6H_{10}ClNO$**



Labaziewicz, H. *et al., J. Chem. Soc., Perkin Trans. 1*, 1979, 2928
There is a risk of explosion if the pressure rises during its vacuum distillation.
See other NITROSO COMPOUNDS

2414. *trans*-2-Chlorocyclohexyl perchlorate

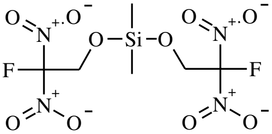
[81971-84-8] **$C_6H_{10}Cl_2O_4$**



See entry ALKYL PERCHLORATES (reference 6)

2415. Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane

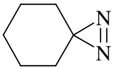
[73526-98-4] **$C_6H_{10}F_2N_4O_{10}Si$**



Neale, R. S., *Ind. Eng,. Chem., Prod. Res. Dev.*, 1980, **19**, 634
This substituted silane (intended as an explosive plasticiser), though relatively stable to heat and impact of a hammer, is exceedingly sensitive to compressive shock. Great care must therefore be exercised in syringing samples of the viscous liquid.
See other ALKYLSILANES, FLUORODINITROMETHYL COMPOUNDS

2416. 3,3-Pentamethylenediazirine

[930-82-5] **$C_6H_{10}N_2$**



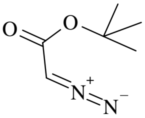
1. Schmitz, E. *et al., Org. Synth.*, 1965, **45**, 85

2. Schmitz, E. *et al., Chem. Ber.*, 1961, **94**, 2168

Small-scale preparation is recommended [1], in view of a previous explosion through superheating of the liquid during distillation at 109°C [2].

See other DIAZIRINES

2417. *tert*-Butyl diazoacetate
[35059-50-8] **$C_6H_{10}N_2O_2$**

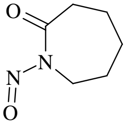


Regitz, M. et al., Org. Synth., 1968, **48**, 36

Vacuum distillation of the compound is potentially hazardous.

See other DIAZO COMPOUNDS

2418. *N*-Nitroso-6-hexanelactam
[35784-01-1] **$C_6H_{10}N_2O_2$**

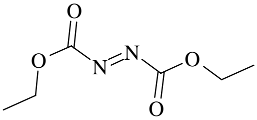


Preparative hazard

See 6-Hexanelactam: Acetic acid, etc.

See other NITROSO COMPOUNDS

2419. Diethyl azoformate (1,2-Bisethoxycarbonyldiazene)
[1972-28-7] **$C_6H_{10}N_2O_4$**



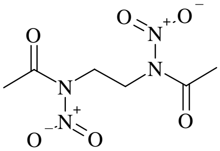
1. US Pat. 3 347 845, 1967
2. Kauer, J. C., *Org. Synth.*, 1963, Coll. Vol. 4, 412
3. Houben Weyl, 1967, 10/2, 809

Shock-sensitive [1], it explodes on heating in a (sealed?) capillary, like its lower homologue. The crude product prepared by chlorine oxidation of the corresponding hydrazide may detonate violently during distillation. This is thought due to either excess chlorine or inadequate washing leaving chloramine byproducts [3]. However, the editor believes the alternative preparation of azodicarboxylates by fuming nitric acid oxidation of the hydrazide [2] can give azide and nitramine impurities; crude methyl ester from this route has also exploded during distillation.

See Dimethyl azoformate

See other AZO COMPOUNDS

2420. *N,N'*-Diacetyl-*N,N'*-dinitro-1,2-diaminoethane
[922-89-4] **$C_6H_{10}N_4O_6$**

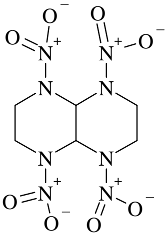


Violent decomposition occurred at 142°C.

See entry DIFFERENTIAL THERMAL ANALYSIS (reference 1)

See other N—NITRO COMPOUNDS

2421. *trans*-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecahydronaphthalene
[83673-81-8] **$C_6H_{10}N_8O_8$**

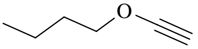


Willer, R. L., *Propellants, Explos. Pyrotech.*, 1983, **8**, 65

A new explosive compound.

See other N—NITRO COMPOUNDS

2422. Butoxyacetylene
[3329-56-4] **$C_6H_{10}O$**

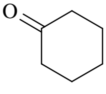


Jacobs, T. L. *et al., J. Amer. Chem. Soc.*, 1942, **64**, 223

Small samples rapidly heated in sealed tubes to around 100°C exploded.

See other ACETYLENIC COMPOUNDS

2423. Cyclohexanone
[108-94-1] **$C_6H_{10}O$**



HCS 1980, 344; *RSC Lab. Hazards Data Sheet No. 80*, 1989

Hydrogen peroxide, Nitric acid

See Hydrogen peroxide: Ketones, etc.

Nitric acid

See Nitric acid: 4-Methylcyclohexanone

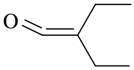
Other reactants

Yoshida, 1980, 152

MRH values calculated for 14 combinations with oxidants are given.

2424. Diethylketene (2-Ethyl-1-butene-1-one)

[24264-08-2] **$C_6H_{10}O$**



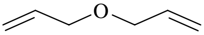
Sorbe, 1968, 118

Like the lower homologue, it readily forms explosive peroxides with air at ambient temperature.

See other PEROXIDISABLE COMPOUNDS

†2425. Diallyl ether (Di-2-propenyl ether)

[557-40-4] **$C_6H_{10}O$**



HCS 1980, 126

Preparative hazard

MCA Case History No. 412

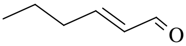
The ether was left exposed to air and sunlight for 2 weeks before distillation, and became peroxidised. During distillation to small bulk, a violent explosion occurred.

See 2-Propen-1-ol: Sulfuric acid

See other ALLYL COMPOUNDS, PEROXIDATION INCIDENTS, PEROXIDISABLE COMPOUNDS

2426. 2-Hexenal

[6728-26-3] **$C_6H_{10}O$**



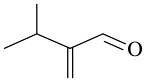
Nitric acid

See Nitric acid: 2-Hexenal

See other PEROXIDISABLE COMPOUNDS

†2427. 2-3-Methyl-2-methylenebutanal (Isopropylacryladehyde)

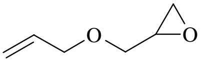
[4417-80-5] **$C_6H_{10}O$**



See other PEROXIDISABLE COMPOUNDS

2428. 1-Allyloxy-2,3-epoxypropane (Allyl glycidyl ether) (2-Propenyloxymethyloxirane)

[106-92-3] **$C_6H_{10}O_2$**



Peroxide test strips

Anon., *Jahresber.*, 1987, 65

Peroxide test strips may not be sufficiently reliable as the sole means of testing for presence of peroxides in a wide range of susceptible liquids.

A sample of the readily peroxidisable allyl ether, tested with a peroxide test strip gave a negative test result, so was charged into a distillation apparatus, but there was a detonation during distillation. It was recommended that an additional test (potassium iodide—acetic acid) should be used unless it is certain that the test strips will give a positive result with a particular peroxide-containing liquid.

See PEROXIDES IN SOLVENTS, PEROXIDISABLE COMPOUNDS

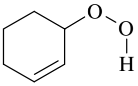
Poly[oxy(methyl)silylene]

See Poly[oxy(methyl)silylene]: 1-Allyloxy-2,3-epoxypropane

See other ALLYL COMPOUNDS, 1,2-EPOXIDES

2429. 2-Cyclohexenyl hydroperoxide

[4845-05-0] **$C_6H_{10}O_2$**



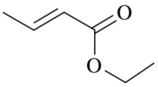
Leleu, *Cahiers*, 1973, (71), 226

Accidental contact of a mixture containing the peroxide with the hot top of the freshly sealed glass container led to an explosion.

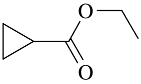
See other ALKYL HYDROPEROXIDES

†2430. Ethyl crotonate

[623-70-1] **$C_6H_{10}O_2$**

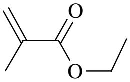


†2431. Ethyl cyclopropanecarboxylate
[4606-07-9] **$C_6H_{10}O_2$**

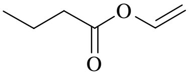


See other STRAINED-RING COMPOUNDS

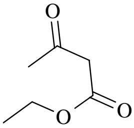
†2432. Ethyl methacrylate
[97-63-2] **$C_6H_{10}O_2$**



†2433. Vinyl butyrate
[123-20-6] **$C_6H_{10}O_2$**



2434. Ethyl acetoacetate (Ethyl 3-oxobutanoate)
[141-97-9] **$C_6H_{10}O_3$**



HCS 1980, 463

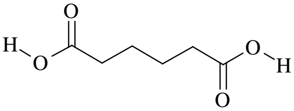
2,2,2-Tris(bromomethyl)ethanol, Zinc

1. Reeder, J. A., U S Pat. 3 578 619, 1971
2. *491M*, 1975, 167

The patent describes the formation of complex metal chelates by treatment of the ketoester simultaneously with an alcohol and a metal to effect trans-esterification and chelate formation by distilling out the by-product ethanol [1]. This process was being applied to produce the zinc chelate of 2-tris(bromomethyl)ethyl acetoacetate, and when 80% of the ethanol had been distilled out (and the internal temperature had increased considerably), a violent decomposition occurred [2]. This presumably involved interaction of a bromine substituent with excess zinc to form a Grignard-type reagent, and subsequent exothermic reaction of this with one or more of the bromo or ester functions present.

See related GRIGNARD REAGENTS

2435. Adipic acid (Hexane-1,6-dioic acid)
[124-04-9] **$C_6H_{10}O_4$**

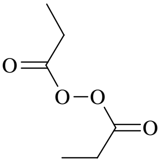


Kaiser, M. A., *Plant/Oper. Progr.*, 1991, **10**(2), 100

After two minor dust explosions in an industrial adipic acid dryer, evidence was obtained that adipic acid forms an iron complex capable of both decarboxylation/ dehydration of adipic acid to cyclopentanone and of catalysing air oxidation, giving exotherms from as low as 135°C.

See other CATALYTIC IMPURITY INCIDENTS, ORGANIC ACIDS, SELF-HEATING AND IGNITION INCIDENTS

2436. Dipropionyl peroxide
[3248-28-0] **$C_6H_{10}O_4$**



Swern, 1971, Vol. 2, 815

Pure material explodes on standing at ambient temperature.

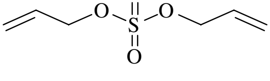
Other reactants

Yoshida, 1980, 317

MRH values calculated for 13 combinations, largely with materials catalysing its decomposition, are given.

See other DIACYL PEROXIDES

2437. Diallyl sulfate
[27063-40-7] **$C_6H_{10}O_4S$**

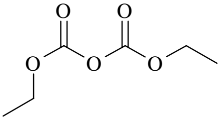


von Braun, J. *et al., Ber.*, 1917, **50**, 293

The explosive decomposition during distillation may well have been caused by polymerisation initiated by acidic decomposition products.

See other ALLYL COMPOUNDS, POLYMERISATION INCIDENTS, SULFUR ESTERS

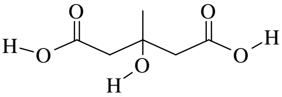
2438. Diethyl dicarbonate (Ethyl pyrocarbonate)
[1609-47-8] **$C_6H_{10}O_5$**



1. Anon., *Univ. Safety Assoc. Safety Digest*, 1991, **42**, 7
2. Scofield, M. A. *University of Arizona Lab. Safety Notes*, 1992, (summer), 1

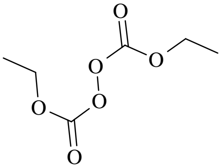
Unopened bottles of this, all originating from the same batch and well within the manufacturer's expiry date, exploded while warming to room temperature. This was attributed to water contamination leading to hydrolysis and carbon dioxide formation, without supporting evidence — a number of other contaminants, both nucleophiles and acids, might catalyse carbon dioxide formation (Editor) [1]. A roughly contemporary report has one, month old, unopened bottle exploding during cool storage and two others bursting during opening. This may be the same tale retold, or more of the same batch. Purchase of minimal quantities and short, refrigerated, storage are recommended [2].
See other GAS EVOLUTION INCIDENTS

2439. 2-Hydroxy-2-methylglutaric acid
[503-49-1] **$C_6H_{10}O_5$**



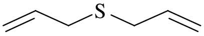
Preparative hazard
See 4-Hydroxy-4-methyl-1,6-heptadiene: Ozone
See other ORGANIC ACIDS

2440. Diethyl peroxydicarbonate
[14666-78-5] **$C_6H_{10}O_6$**



An oil of extreme instability when impure, and sensitive to heat or impact, exploding more powerfully than dibenzoyl peroxide.
See entry PEROXYCARBONATE ESTERS

2441. Diallyl sulfide
[592-88-1] **$C_6H_{10}S$**

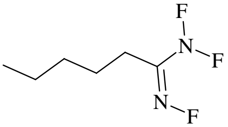


N-Bromosuccinimide

See N-HALOIMIDES: ALCOHOLS ETC.

See other ALLYL COMPOUNDS

2442. *N,N,N'*-Trifluorohexanamidine
[31330-22-0] **$C_6H_{11}F_3N_2$**

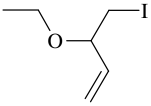


Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3096—3097

A shock-sensitive explosive.

See other N,N,N'-TRIFLUOROAMIDINES

2443. 2-Ethoxy-1-iodo-3-butene
[13957-21-6] **$C_6H_{11}IO$**



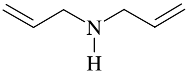
Trent, J. *et al., Chem. Eng. News*, 1966, **44**(33), 7

During a 1 g mol-scale preparation by a published method from butadiene, ethanol, iodine and mercury oxide, a violent explosion occurred while ethanol was being distilled off at 35°C under slight vacuum. The cause of the explosion could not be established, and several smaller-scale preparations had been uneventful.

See other IODINE COMPOUNDS

See related HALOALKENES

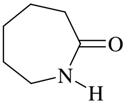
†2444. Diallylamine
[124-02-7] **$C_6H_{11}N$**



HCS 1980, 356

See other ALLYL COMPOUNDS, ORGANIC BASES

2445. Caprolactam (6-Hexanelactam)
[105-60-2] **$C_6H_{11}NO$**



HCS 1980, 258

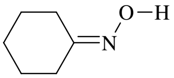
Acetic acid, Dinitrogen trioxide

Huisgen, R. *et al., Ann.*, 1952, **575**, 174—197

During preparation of the *N*-nitroso derivative from the lactam in acetic acid solution, the treatment with dinitrogen trioxide must be very effectively cooled to prevent explosive decomposition.

2446. Cyclohexanone oxime (Hydroximinocyclohexane)

[100-64-1] **$C_6H_{11}NO$**



HCS 1980, 345

1. Ullmann, 1986, **A5** 34
2. Thayer, A., Chem. Eng. News, 2002, 80(38), 18

It can decompose violently, for unknown reasons, during vacuum distillation (probably exothermic Beckmann rearrangement and subsequent polymerisation - Editor) [1]. A rail tank-car of the oxime has exploded during transport [2].

Oleum (fuming sulfuric acid)

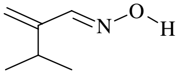
Ale, B. J. M., *Proc. 3rd Intl. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 4, 1541—1550, Basle, SSCI, 1980

During startup of the Beckmann rearrangement stage in the caprolactam process, a mixture of caprolactam and oleum is preheated to operating temperature, then oxime feed and cooling are begun. On one occasion, the exothermic rearrangement (Q = 230.8 kJ/mol, 2.04 kJ/g of oxime) failed to start, and the temperature decreased. On application of steam to the cooler to start the reaction, the reactor vessel burst. At temperatures above 150—160°C, oleum oxidises the oxime with evolution of carbon dioxide and sulfur trioxide. An investigation of the operating stability of the reactor system and transient behaviour during startup allowed safe starting procedures to be clearly defined.

See other GAS EVOLUTION INCIDENTS, OXIMES

2447. 2-Isopropylacrylaldehyde oxime

[ ] **$C_6H_{11}NO$**



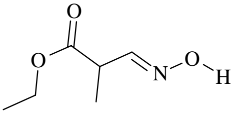
Marvel, C. S. *et al., J. Amer. Chem. Soc.*, 1950,**72**, 5408—5409

Hydroquinone must be added to the oxime before distillation, to prevent formation and subsequent violent decomposition of a peroxide (there being 2 susceptible hydrogen atoms in the molecule).

See other OXIMES, PEROXIDISABLE COMPOUNDS

2448. Ethyl 2-formylpropionate oxime

[ ] **$C_6H_{11}NO_3$**



Hydrogen chloride (?)

Loftus, F., private comm., 1972

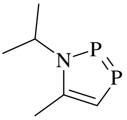
The formyl ester and hydroxylamine were allowed to react in ethanol, which was then removed by vacuum evaporation at 40°C. The dry residue decomposed violently 5 min later. Analysis of the residue suggested that the oxime had undergone an exothermic Beckmann rearrangement, possibly catalysed by traces of hydrogen chloride in the reaction residue.

See Butyraldehyde oxime

See other CATALYTIC IMPURITY INCIDENTS, OXIMES

2449. 5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole (3(1-Methylethyl)-4-methyldiphosphazole)

[126330-30-1] **$C_6H_{11}NP_2$**



Gueth, W., *New J. Chem.* 1989, **13**(4—5) 309

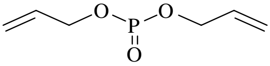
Extremely pyrophoric

See other PYROPHORIC MATERIALS

See related ALKYLPHOSPHINES

2450. Diallyl phosphite (Di-2-propenyl phosphonite)

[23679-20-1] **$C_6H_{11}O_3P$**



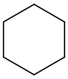
Houben-Weyl, 1964, Vol. 12.2, 22

The ester is liable to explode during distillation unless thoroughly dry allyl alcohol is used for the preparation, and if more than 60% of the product is distilled over. Acid-catalysed polymerisation is probably involved.

See other ALLYL COMPOUNDS, PHOSPHORUS ESTERS, POLYMERISATION INCIDENTS

†2451. Cyclohexane

[110-82-7] **C_6H_{12}**



(*MCA SD-68*, 1957); *FPA H25*, 1974; *HCS 1980*, 342; *RSC Lab. Hazards Data Sheet No. 54*, 1986

Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Hydrocarbons

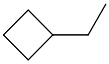
Other reactants

Yoshida, 1980, 153

MRH values calculated for 14 combinations with oxidants are given.

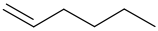
†2452. Ethylcyclobutane

[4806-61-5] **C_6H_{12}**



†2453. 1-Hexene

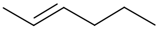
[592-41-6] **C_6H_{12}**



See other ALKENES

†2454. 2-Hexene

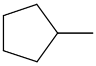
[592-43-8] **C_6H_{12}**



See other ALKENES

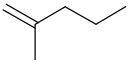
†2455. Methylcyclopentane

[96-37-7] **C_6H_{12}**



†2456. 2-Methyl-1-pentene

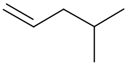
[763-29-1] **C_6H_{12}**



See other ALKENES

†2457. 4-Methyl-1-pentene

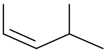
[691-37-2] **C_6H_{12}**



See other ALKENES

†2458. *cis*-4-Methyl-2-pentene

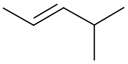
[691-38-3] **C_6H_{12}**



See other ALKENES

†2459. *trans*-4-Methyl-2-pentene

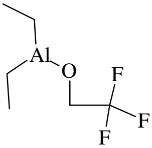
[4461-48-7] **C_6H_{12}**



See other ALKENES

2460. Diethylaluminium 2,2,2-trifluoroethoxide

[116778-64-4] **$C_6H_{12}AlF_3O$**

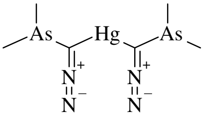


Malpass, D. B., *Chem. Eng. News*, 1990, **68**(14), 2

This compound was found, on investigation of an explosion in a syringe during transfer, to have a decomposition energy equivalent to that of commercial explosives. Slow decomposition, even at room temperature, becomes explosive above 100°C. Shock sensitive. Stable as hydrocarbon solution below 25% concentration. Recommended that this and related compounds be handled only in such solution.

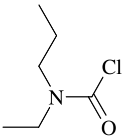
See FLUORINATED ORGANOLITHIUM COMPOUND
See related ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

2461. Bis(dimethylarsinyldiazomethyl)mercury
[63382-64-9] **$C_6H_{12}As_2HgN_4$**



Glozbach, E. *et al., J. Organomet. Chem.*, 1977, **132**, 359
It is explosive.
See other DIAZO COMPOUNDS, MERCURY COMPOUNDS
See related ALKYLNON-METALS

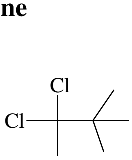
2462. *N*-Ethyl-*N*-propylcarbamoyl chloride
[98456-61-2] **$C_6H_{12}ClNO$**



Water

Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 78
The chloride (60 l) and 2 volumes of water were mixed ready for subsequent addition of alkali to effect controlled hydrolysis. Before alkali was added, the internal temperature rose from 15 to 25° during 30 min, and then to 35°C in 5 min, when gas was suddenly evolved. This was attributed to the effect of liberated hydrochloric acid causing autocatalytic acceleration of the hydrolysis and then rapid release of carbon dioxide arising from decarboxylation of the carbamic acid. Hydrolysis by addition of the chloride to excess alkali would prevent the gas evolution.
See other ACYL HALIDES, GAS EVOLUTION INCIDENTS

2463. 2,2-Dichloro-3,3-dimethylbutane
[594-84-3] **$C_6H_{12}Cl_2$**



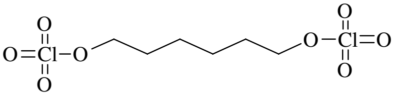
Sodium hydroxide

1. Bartlett, P. D. *et al., J. Amer. Chem. Soc.*, 1942, **64**, 543
2. Kocienski, P. J., *J. Org. Chem.*, 1974, **39**, 3285—3286

A previous method [1] of preparing 3,3-dimethylbutyne by dehydrochlorination of the title compound in a sodium hydroxide melt is difficult to control and hazardous on the

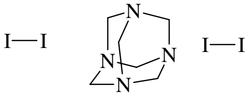
large scale. Use of potassium *tert*-butoxide as base in DMSO is a high-yielding, safe and convenient alternative method of preparation of the alkyne [2].
See Dimethyl sulfoxide: Metal alkoxides
See other HALOALKANES

2464. 1,6-Hexanediyl perchlorate
[95407-64-0] **$C_6H_{12}Cl_2O_8$**



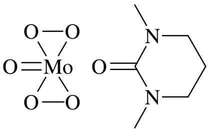
See entry ALKYL PERCHLORATES (reference 6)

2465. Hexamethylenetetramine tetraiodide
[12001-65-9] **$C_6H_{12}I_4N_4$**



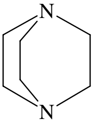
Merck, 1976, 779
The hexamine—iodine complex deflagrates at 138°C.
See other IODINE COMPOUNDS

2466. Oxodiperoxy(1,3-dimethyl-2,4,5,6-tetrahydro-2-1*H*)-pyrimidinone)molybdenum
[128568-96-7] **$C_6H_{12}MoN_2O_6$**



Paquette, L. A. *et al., Chem. Eng. News*, 1992, **70**(37), 2
A well dried sample of this complex exploded violently when pushed through a funnel with a steel spatula. The pyridine adduct, which was being prepared, is claimed to be a useful, safe, oxidant, replacing the hexamethylphosphoramide complex of MoO_5 (ibid.).
See other METAL PEROXIDES

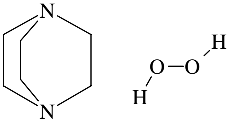
2467. 1,4-Diazabicyclo[2.2.2]octane
[280-57-9] **$C_6H_{12}N_2$**



An exceptionally strong base.

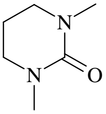
Carbon
See Carbon: 1,4-Diazabicyclo[2.2.2]octane
Cellulose nitrate
See CELLULOSE NITRATE: Amines
Hydrogen peroxide
See NEXT BELOW
See other ORGANIC BASES

2468. 1,4-Diazabicyclo[2.2.2]octane hydrogen peroxidate [39810-25-8] $C_6H_{12}N_2.H_2O_2$



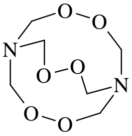
Davies, A. G. *et al., J. Chem. Soc., Perkin Trans. 2*, 1981, 1512
A sample of the 1:1 complex exploded while being dried overnight in a desiccator.
See other CRYSTALLINE HYDROGEN PEROXIDATES

2469. 1,3-Dimethylhexahydropyrimidone (Dimethylpropyleneurea) [7226-23-5] $C_6H_{12}N_2O$



Chromium trioxide
See Chromium trioxide: 1,3-Dimethylhexahydropyrimidone

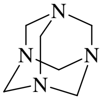
2470. 1,6-Diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane ('Hexamethylenetriperoxydiamine') [283-66-9] $C_6H_{12}N_2O_6$



Alone, or Bromine, or Sulfuric acid
1. Leulier, *J. Pharm. Chim.*, 1917, **15**, 222—229
2. Lefebvre, M. H. *et al., Chem. Abs.* 2004, **141**, 176244b

The compound, precipitated by interaction of hexamethylene tetramine and acidic 30% hydrogen peroxide, is a heat- and shock-sensitive powerful explosive when dry, much more shock sensitive than mercury fulminate. It explodes in contact with bromine or sulfuric acid [1]. It has been assessed as an explosive [2].
See other CYCLIC PEROXIDES

2471. Hexamethylenetetramine (1,3,5,7-Tetraazatricyclo[3.3.1.1^{3,7}]decane)
[100-97-0] **$C_6H_{12}N_4$**



Finely powdered dry hexamine is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

Acetic acid, Acetic anhydride, Ammonium nitrate, Nitric acid
See Nitric acid: Acetic anhydride, Hexamethylenetetramine acetate

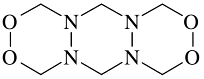
1-Bromopentaborane(9)
See 1-Bromopentaborane(9): Air, or Hexamethylenetetramine

Hydrogen peroxide
See 1,6-Diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane

Iodine
See Hexamethylenetetramine tetraiodide

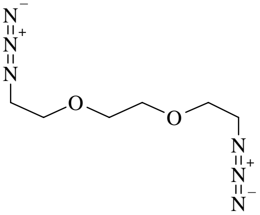
Iodoform
See Iodoform: Hexamethylenetetramine
See other ORGANIC BASES

2472. 4a,8a,9a,10a-Tetraaza-2,3,6,7-tetraoxaperhydroanthracene
[262-38-4] **$C_6H_{12}N_4O_4$**



Katritzky, A. R. *et al., J. Chem. Soc., Perkin Trans. 2*, 1979, 1136
The bis-peroxy tricyclic heterocycle explodes at 120°C.
See other CYCLIC PEROXIDES

2473. 1,2-Bis(2-azidoethoxy)ethane
[59559-06-7] **$C_6H_{12}N_6O_2$**



Ethanol, Hydrogen sulfide

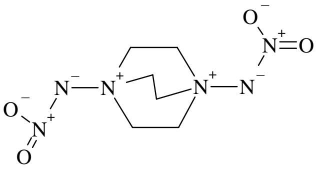
Anon., *Lab. Accid. Higher Educ*. Item 32, HSE, Barking, 1987

During the reduction of the azide in ethanol with hydrogen sulfide (no regulation other than main cylinder valve) under reflux (with insufficient flow of condenser water), the mixture apparently overheated, then exploded violently.

See other ORGANIC AZIDES

2474. 1,4-Diazabicyclo[2.2.2]octane 1,4-bis(nitroimidate)

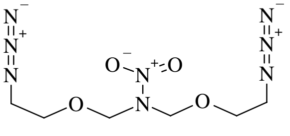
[51470-74-7] **$C_6H_{12}N_6O_4$**



See *N*-AZOLIUM NITROIMIDATES

2475. Bis(2-azidoethoxymethyl)nitramine (*N,N*' Bis[(2-azidoethoxy)methyl]-*N,N*'-dintroethane-1,2-diamine)

[84487-87-6] **$C_6H_{12}N_8O_4$**

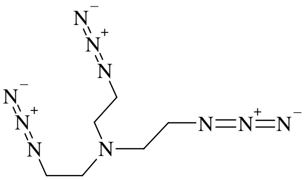


See entry ENERGETIC COMPOUNDS

See other N—NITRO COMPOUNDS, ORGANIC AZIDES

2476. Tris(2-azidoethyl)amine

[84928-99-4] **$C_6H_{12}N_{10}$**

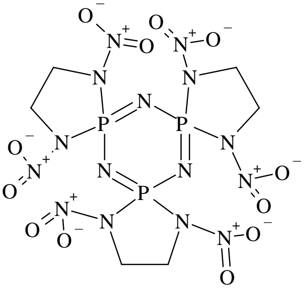


See entry ENERGETIC COMPOUNDS

See other ORGANIC AZIDES

2477. 1,1,3,3,5,5-Tris-spiro(*N,N'*-dinitroethylenediamino)cyclotriphosphazene (1,4,8,11,14,17-Hexanitro-1,4,6,8,11,12,14,17,18-nonaaza-5λ^5,7λ^5,13λ^5-triphosphatatrispiro[4.1.4.1.4.1]octadeca-5,7(12),13(18)-triene)

[155793-91-2] **$C_6H_{12}N_{15}O_{12}P_3$**



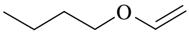
1. Paritosh, D. R. *et al., Chem. Abs.*, 1994, **121**, 35869j; U.S. Pat. Appl. 42,229
2. Paritosh, D. R. *et al., Phosphorus, Sulfur, Silicon Relat. Elem..*, 1994, **90**(1-4), 175

This and several other compounds with fewer nitro groups and partial replacement of the spiro rings by halogen are patented as explosives.

See other N—NITRO COMPOUNDS

†2478. Butyl vinyl ether

[111-34-2] **$C_6H_{12}O$**



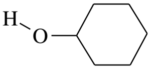
Glikin, M. A. *et al., Chem. Abs.*, 1978, **89**, 30115

'Explosion hazard of industrial synthesis of butyl vinyl ether' (title only translated).

See other PEROXIDISABLE COMPOUNDS

2479. Cyclohexanol

[108-93-0] **$C_6H_{12}O$**



FPA H91, 1980; *HCS 1980*, 343

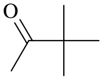
Other reactants

Yoshida, 1980, 151

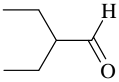
MRH values calculated for 12 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
Nitric acid: Alcohols	MRH 5.86/81
See Chromium trioxide: Alcohols	MRH 2.55/92

†2480. 3,3-Dimethyl-2-butanone
[75-97-8] **$C_6H_{12}O$**

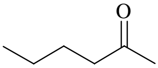


†2481. 2-Ethylbutanal
[97-96-1] **$C_6H_{12}O$**



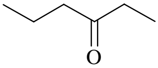
See other PEROXIDISABLE COMPOUNDS

†2482. 2-Hexanone
[591-78-6] **$C_6H_{12}O$**

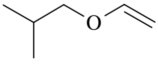


HCS 1980, 643

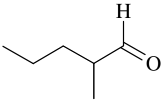
†2483. 3-Hexanone
[589-38-8] **$C_6H_{12}O$**



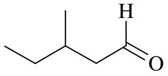
†2484. Isobutyl vinyl ether
[109-53-5] **$C_6H_{12}O$**



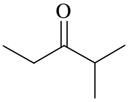
†2485. 2-Methylpentanal
[123-15-9] **$C_6H_{12}O$**



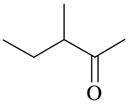
†2486. 3-Methylpentanal
[15877-57-3] **$C_6H_{12}O$**



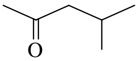
†2487. 2-Methyl-3-pentanone
[565-69-5] **$C_6H_{12}O$**



†2488. 3-Methyl-2-pentanone
[565-61-7] **$C_6H_{12}O$**



†2489a. 4-Methyl-2-pentanone
[108-10-1] **$C_6H_{12}O$**



FPA H97, 1981; *HCS 1980*, 576

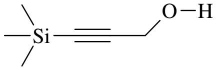
1. Smith, G. H., *Chem. & Ind.*, 1972, 291
2. Bretherick. L., *Chem. & Ind.*, 1972, 363

4-Methyl-2-pentanone had not been considered prone to autoxidation, but an explosion during prolonged and repeated aerobic hot evaporation of the solvent [1] was attributed to formation and explosion of a peroxide [2].

Other reactants
Yoshida, 1980, 363
MRH values calculated for 13 combinations with oxidants are given.

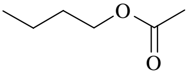
Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.
See other PEROXIDISABLE COMPOUNDS

2489b. 3-Trimethylsilyl-2-propyn-1-ol
[5272-36-6] **$C_6H_{12}OSi$**



Novokshonov, V. V. et al., Russ. J. Org. Chem., 1998, 34(10), 1426
During attempted vacuum distillation the compound polymerised explosively.
See other ACETYLENIC COMPOUNDS

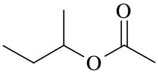
†2490. Butyl acetate
[123-86-4] **$C_6H_{12}O_2$**



FPA H116, 1982; *HCS 1980*, 233

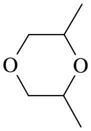
Potasium *tert*-butoxide
See Potassium *tert*-butoxide: Acids, etc.

†2491. 2-Butyl acetate
[105-46-4] **$C_6H_{12}O_2$**

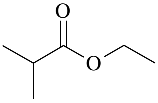


HCS 1980, 234

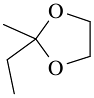
†2492. 2,6-Dimethyl-1,4-dioxane
[10138-17-7] **$C_6H_{12}O_2$**



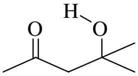
†2493. Ethyl isobutyrate
[97-62-1] **$C_6H_{12}O_2$**



†2494. 2-Ethyl-2-methyl-1,3-dioxolane
[126-39-6] **$C_6H_{12}O_2$**

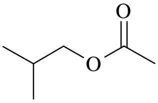


†2495. 4-Hydroxy-4-methyl-2-pentanone
[123-42-2] **$C_6H_{12}O_2$**



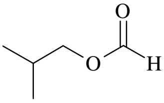
HCS 1980, 355

†2496. Isobutyl acetate
[110-19-0] **$C_6H_{12}O_2$**



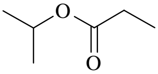
HCS 1980, 567

†2497. Isopentyl formate
[110-45-2] **$C_6H_{12}O_2$**



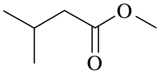
HCS 1980, 564

†2498. Isopropyl propionate
[637-78-5] **$C_6H_{12}O_2$**



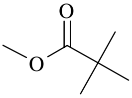
†2499. Methyl isovalerate

[556-24-1] **$C_6H_{12}O_2$**



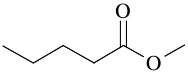
†2500. Methyl pivalate

[598-98-1] **$C_6H_{12}O_2$**



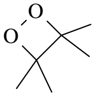
†2501. Methyl valerate

[624-24-8] **$C_6H_{12}O_2$**



2502. Tetramethyl-1,2-dioxetane

[35856-82-7] **$C_6H_{12}O_2$**



Kopecky, K. R. *et al., Can. J. Chem.*, 1975, **53**, 1107

Several explosions occurred in vacuum-sealed samples kept at ambient temperature. Storage under air at —20°C, or as solutions up to 2 Mol appear safe.

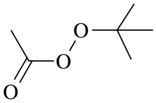
See 3,3-Dimethyl-1,2-dioxetane

See DIOXETANES

See other CYCLIC PEROXIDES

2503. *tert*-Butyl peroxyacetate

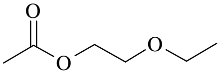
[107-71-1] **$C_6H_{12}O_3$**



1. Martin, J. H., *Ind. Eng. Chem.*, 1960, **52**(4), 49A
2. Castrantas, 1965, 16
3. *CHETAH*, 1990, 188

The peroxyester explodes with great violence when rapidly heated to a critical temperature. Previous standard explosivity tests had not shown this behaviour. The presence of benzene (or preferably a less toxic solvent) as diluent prevents the explosive decomposition, but if the solvent evaporates, the residue is dangerous [1]. The pure ester is also shock-sensitive and detonable, but the commercial 75% solutions are not [2]. However, a 75% benzene solution has been exploded with a detonator, though not by mechanical shock [3].
See other PEROXYESTERS

2505. 2-Ethoxyethyl acetate
[111-15-9] **$C_6H_{12}O_3$**

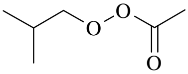


HCS 1980, 461

1. Anon., private comm., 1975
2. Author's comments

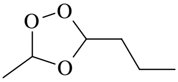
Mild explosions have occurred at the end of technical-scale distillations of 'ethyl glycol acetate' in a copper batch still about 20 min after the kettle heater was shut off. It is possible that air was drawn into the distillation column as it cooled, creating a flammable mixture, but no mechanism for ignition could be established. Oxidation studies did not indicate the likely formation of high peroxide concentrations in the liquid phase of this ether—ester [1]. It seems remotely possible that small amounts of dioxane (formed by dehydration of traces of ethylene glycol) or of acetaldehyde (arising from traces of ethanol or from cracking of the ester, catalysed perhaps by copper), and both having very low autoignition temperatures, may have been involved in the incidents [2].

†2506. Isobutyl peroxyacetate
[55153-36-1] **$C_6H_{12}O_3$**



See other PEROXYESTERS

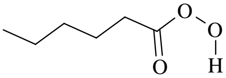
2507. *trans*-2-Hexene ozonide (3-Methyl-5-propyl-1,2-4-trioxolane)
[ ] **$C_6H_{12}O_3$**



Loan, L. D. *et al., J. Amer. Chem. Soc.*, 1965, **87**, 41

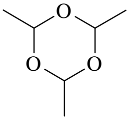
Attempts to get C and H analyses by combustion of the ozonides of 2-butene, 2-pentene and 2-hexene caused violent explosions, though oxygen analyses were uneventful.
See other OZONIDES

2508. Peroxyhexanoic acid
[5106-46-7] **$C_6H_{12}O_3$**



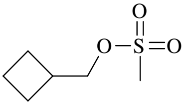
Swern, D., *Chem. Rev.*, 1949, **45**, 10
Fairly stable at ambient temperature, it explodes and ignites on rapid heating.
See other PEROXYACIDS

†2509. 2,4,6-Trimethyltrioxane
[123-63-7] **$C_6H_{12}O_3$**



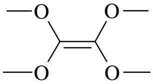
Nitric acid
See Nitric acid: 2,4,6-Trimethyltrioxane

2510. Cyclobutylmethyl methanesulfonate
[22524-45-4] **$C_6H_{12}O_3S$**



Explodes during distillation at 81—89°C/0.8 mbar.
See entry SULFONIC ACID ESTERS
See other SULFUR ESTERS

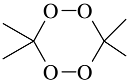
2511. Tetramethoxyethylene
[1069-12-1] **$C_6H_{12}O_4$**



Preparative hazard
See 1,2,3,4-Tetrachloro-7,7-dimethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene

2512. 3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane

[1073-91-2] **$C_6H_{12}O_4$**



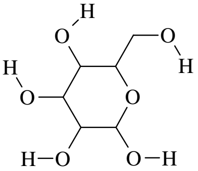
Baeyer, A. *et al., Ber.*, 1900, **33**, 858

Action of hydrogen peroxide or permonosulfuric acid on acetone produces this dimeric acetone peroxide, which explodes violently on impact, friction or rapid heating.

See other CYCLIC PEROXIDES

2513. Glucose

[50-99-7] **$C_6H_{12}O_6$**



Energy of decomposition (in range 224—330°C) measured as 0.406 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkali

See SUGARS

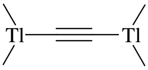
Potassium nitrate, Sodium peroxide

See Sodium peroxide: Glucose, Potassium nitrate

See other REDUCANTS

2514. Bis(dimethylthallium)acetylide

[ ] **$C_6H_{12}Tl_2$**



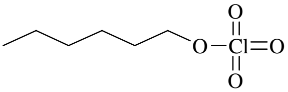
Nast, R. *et al., J. Organomet. Chem.*, 1966, **6**, 461

Extremely explosive, heat- and friction-sensitive.

See related ALKYLMETALS, METAL ACETYLIDES

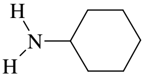
2515. Hexyl perchlorate

[52936-24-0] **$C_6H_{13}ClO_4$**



See entry ALKYL PERCHLORATES (reference 6)

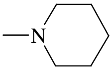
†2516. Cyclohexylamine
[108-91-8] **$C_6H_{13}N$**



HCS 1980, 347

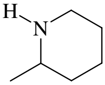
Nitric acid
See NITRIC ACID: CYCLOHEXYLAMINE
See other ORGANIC BASES

†2517. 1-Methylpiperidine
[626-67-5] **$C_6H_{13}N$**



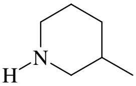
See other ORGANIC BASES

†2518. 2-Methylpiperidine
[109-05-7] **$C_6H_{13}N$**



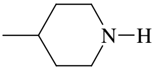
See other ORGANIC BASES

†2519. 3-Methylpiperidine
[626-56-2] **$C_6H_{13}N$**



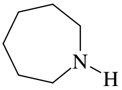
See other ORGANIC BASES

†2520. 4-Methylpiperidine
[626-58-4] **$C_6H_{13}N$**



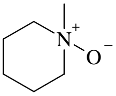
See other ORGANIC BASES

†2521. Perhydroazepine (Hexamethyleneimine)
[111-49-9] **$C_6H_{13}N$**



See other ORGANIC BASES

2522. *N*-Methylpiperidine *N*-oxide
[17206-00-7] **$C_6H_{13}NO$**

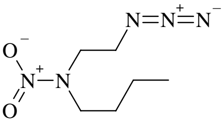


Cope, A. C. *et al., J. Amer. Chem. Soc.*, 1960, **82**, 4656

This amine oxide is thermally surprisingly stable, decomposing explosively at 215°C.

See other N-OXIDES

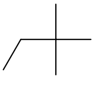
2523. *N*-Butyl-*N*-2-azidoethylnitramine
[84928-98-3] **$C_6H_{13}N_5O_2$**



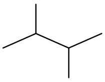
See entry ENERGETIC COMPOUNDS

See other N—NITRO COMPOUNDS, ORGANIC AZIDES

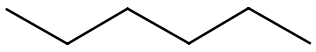
†2524. 2,2-Dimethylbutane
[75-83-2] **C_6H_{14}**



†2525. 2.3-Dimethylbutane
[79-29-8] **C_6H_{14}**



†2526. Hexane
[110-54-3] **C_6H_{14}**

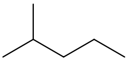


FPA H83, 1979; *HCS 1980*, 533 (covers isomers); *RSC Lab. Hazards Data Sheet No.63*, 1987

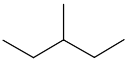
Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Hydrocarbons

Other reactants
Yoshida, 1980, 326
MRH values calculated for 13 combinations with oxidants are given.

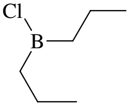
†2527. Isohexane (2-Methylpentane)
[107-83-5] **C_6H_{14}**



†2528. 3-Methylpentane
[96-14-0] **C_6H_{14}**

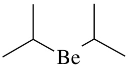


2529. Chlorodipropylborane
[22086-53-9] **$C_6H_{14}BCl$**



Leleu, *Cahiers*, 1977, (88), 365
It ignites in air
See other ALKYLHALOBORANES

2530. Diisopropylberyllium
[15721-33-2] **$C_6H_{14}Be$**



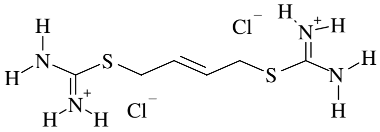
Water

Coates, G. E. *et al., J. Chem. Soc.*, 1954, 22

Uncontrolled reaction with water is explosive.

See other ALKYLMETALS

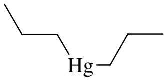
2531. 1,4-Bis(isothiouronio)-2-butene dichloride
[67405-47-4] $C_6H_{14}Cl_2N_4S_2$



Harrp, D. N. *et al., Org. Prep. Proceed. Int.*, 1978, **10**, 13

Crystallisation from 95% ethanol is strongly exothermic.

2532. Dipropylmercury
[628-85-3] $C_6H_{14}Hg$



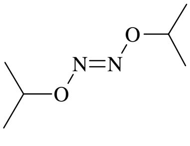
Iodine

Whitmore, 1921, 100

Interaction is violent.

See other ALKYLMETALS, MERCURY COMPOUNDS

2533. Diisopropyl hyponitrite (Bis(2-propyloxy)diazene)
[82522-47-2]; E-[86886-16-0] $C_6H_{14}N_2O_2$



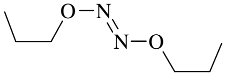
Ogle, C. A. *et al., J. Org. Chem.*, 1983, **48**, 3729

It detonated violently when deliberately struck.

See other DIALKYL HYPONITRITES

2534. Dipropyl hyponitrite (Bis(propyloxy)diazene)

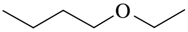
[ ] **$C_6H_{14}N_2O_2$**



See entry DIALKYL HYPONITRITES

†2535. Butyl ethyl ether

[628-81-9] **$C_6H_{14}O$**

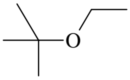


HCS 1980, 473

See other PEROXIDISABLE COMPOUNDS

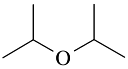
†2536. *tert*-Butyl ethyl ether

[637-92-3] **$C_6H_{14}O$**



†2537. Diisopropyl ether

[108-20-3] **$C_6H_{14}O$**



FPA H101, 1981; *HCS 1980*, 579

1. Anon., *Chem. Eng. News*, 1942, **20**, 1458
2. *MCA Case Histories Nos. 603, 1607*
3. Douglass, I. B., *J. Chem. Educ.*, 1963, **40**, 469
4. Rieche, A. *et al., Ber.*, 1942, **75**, 1016
5. Hamstead, A. C. *et al., J. Chem. Eng. Data.*, 1960, **5**, 583; *Ind. Eng. Chem.*, 1961, **53**(2), 63A
6. Walton, G. C., *CHAS Notes*, 1988, **6**, 3
7. Demer, F. R., *University of Arizona Lab. Safety Notes*, 1992, winter

There is a long history of violent explosions involving peroxidised diisopropyl ether, with initiation by disturbing a drum [1], unscrewing a bottle cap [2], or accidental impact [3]. This ether, with two highly susceptible hydrogen atoms adjacent to the oxygen link, is extremely readily peroxidised after only a few hours' exposure to air, initially to a dihydroperoxide which disproportionates to dimeric and trimeric acetone peroxides. These separate from solution and are highly explosive [4]. Presence of a crystalline solid in a sample of the ether should be a cause for great concern, no attempt being made to open the container. Professional assistance should be sought for the safe disposal of substantially peroxidised samples. It has been reported that the ether may be inhibited completely against peroxide formation for a considerable time by addition of *N*-benzyl-4-aminophenol at 16 ppm, or by addition of diethylenetriamine, triethylenetetramine or tetraethylenepentamine at 50 ppm [5]. Further information on the extreme hazards of peroxidised diisopropyl ether is presented, with directions for safe disposal in a remote location by controlled explosion. The dry crystalline peroxide is photo-sensitive and will detonate on exposure to sunlight. Four additional literature references are included [6]. Evaporation of solvent from reactions performed in isopropyl ether of unknown history may, as for other ethers, concentrate peroxides to explosion, even though no solid is seen [7].

See 3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, *and* 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane,

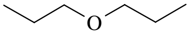
See also ETHERS

Propionyl chloride

See Propionyl chloride: Diisopropyl ether

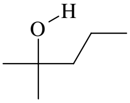
See other PEROXIDATION INCIDENTS, PEROXIDISABLE COMPOUNDS

†2538. Dipropyl ether
[111-43-3] **$C_6H_{14}O$**

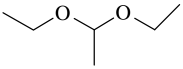


See other PEROXIDISABLE COMPOUNDS

†2539. 2-Methyl-2-pentanol
[590-36-3] **$C_6H_{14}O$**



†2540. 1,1-Diethoxyethane (Diethyl acetal)
[105-57-7] **$C_6H_{14}O_2$**



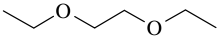
Mee, A. J., *School Sci. Rev.*, 1940, **22**(86), 95

A peroxidised sample exploded violently during distillation.

See other PEROXIDISABLE COMPOUNDS

†2541. 1,2-Diethoxyethane

[629-14-1] **$C_6H_{14}O_2$**

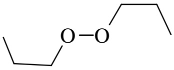


HCS 1980, 400

See other PEROXIDISABLE COMPOUNDS

2542. Dipropyl peroxide

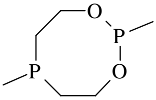
[29914-92-9] **$C_6H_{14}O_2$**



Swern, 1972, Vol. 3, 21
Unexpected explosions have occurred with dipropyl peroxides.
See other DIALKYL PEROXIDES

2543. 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclooctane

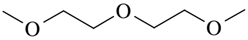
[79251-56-2; 79251-57-3] cis-, trans-, resp. $C_6H_{14}O_2P_2$



Piccini-Leopardi, C. *et al., J. Chem. Soc., Perkin Trans 2*, 1986, 85—92
The isomers could not be separated by distillation at 65—68°C/0.07 mbar, and bath temperatures above 120°C caused explosions.
See related ALKYLPHOSPHINES, PHOSPHORUS ESTERS

2544. Bis-(2-methoxyethyl) ether

[111-96-6] **$C_6H_{14}O_3$**

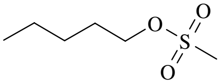


'Diglyme Properties and Uses', Brochure, London, ICI, 1967
Details of properties, applications and safe handling are given. Light, heat and oxygen (air) promote formation of potentially explosive peroxides. These may be removed by stirring with a suspension of iron oxide in aqueous alkali.

Metal hydrides
Lithium tetrahydroaluminate: Bis(2-methoxyethyl) ether
See Aluminium hydride: Carbon dioxide, etc.
See other PEROXIDISABLE COMPOUNDS

2545. 1-Pentyl methanesulfonate

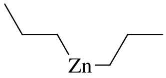
[6968-20-3] **$C_6H_{14}O_3S$**



It decomposes vigorously at 185°C.
See entry SULFONIC ACID ESTERS
See other SULFUR ESTERS

2546. Dipropylzinc

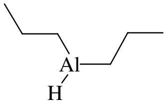
[628-91-1] **$C_6H_{14}Zn$**



Ellern, 1968, 24
It ignites in air if exposed on an extended surface.
See other DIALKYLZINCS

2547. Dipropylaluminium hydride

[2036-15-9] **$C_6H_{15}Al$**

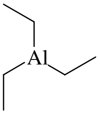


HCS 1980, 444

See entry ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

†2548. Triethylaluminium

[97-93-8] **$C_6H_{15}Al$**



HCS 1980, 929

It ignites in air.
See TRIALKYLALUMINIUMS

Alcohols MRH Methanol, 1.45/46
Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **53**(1), 54A
Interaction of methanol, ethanol and 2-propanol with the undiluted trialkylaluminium is explosive, while *tert*-butanol reacts vigorously.
See ALKYLALUMINIUM DERIVATIVES

Carbon tetrachloride MRH 1.51/85

Reineckel, H., *Angew. Chem. (Intern. Ed.)*, 1964, **3**, 65

A mixture prepared at 0°C with a 3:1 molar excess of halocarbon exploded violently soon after removal of the ice bath. Formation of a 1:1 chlorine-bridged adduct was assumed.

See ALKYLALUMINIUM DERIVATIVES: Halocarbons

Dimethylformamide MRH 1.38/66

'DMF Brochure', Billingham, ICI, 1965

A mixture of the amide solvent and triethylaluminium explodes when heated.

Other reactants

Yoshida, 1980, 248

MRH values calculated for 14 combinations, largely with oxidants, are given.

Tris(pentafluorophenyl)boron

Pohlmann, J. L. W. *et al., Z. Naturforsch.*, 1965, **20b**(1), 5

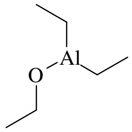
A mixture detonated on warming to 70°C.

See METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

See other ALKYLMETALS, TRIALKYLALUMINIUMS

2549. Diethylethoxyaluminium

[1586-92-1] **$C_6H_{15}AlO$**



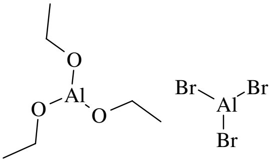
Dangerous Loads, 1972

The pure material, or solutions of above 20% concentration, ignite in air.

See other ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

2550. Triethoxydialuminium tribromide

[65232-69-1] **$C_6H_{15}Al_2Br_3O_3$**



Air, or Ethanol, or Water

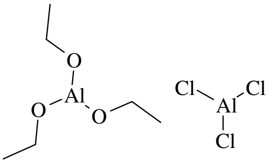
Anon., *Chem. Eng. Progr.*, 1966, **62**(9), 128

It ignites in air and explodes with ethanol and water.

See related ALKYLALUMINIUM ALKOXIDES AND HYDRIDES, METAL HALIDES

2551. Triethyldialuminium trichloride

[12075-68-2] **$C_6H_{15}Al_2Cl_3$**



HCS 1980, 466

Carbon tetrachloride

Reineckel, H., *Angew. Chem. (Intern. Ed.)*, 1964, **3**, 65

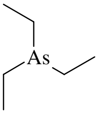
A mixture exploded when warmed to room temperature.

See other ALKYLALUMINIUM HALIDES

See related METAL HALIDES

2552. Triethylarsine

[617-75-4] **$C_6H_{15}As$**



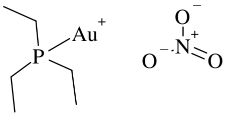
Sidgwick, 1950, 762

It inflames in air.

See other ALKYLNON-METALS

2553. Triethylphosphinegold nitrate

[14243-51-7] **$C_6H_{15}AuNO_3P$**



Coates, G. E. *et al., Aust. J. Chem.*, 1966, **19**, 541

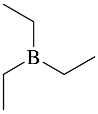
After thorough desiccation, the crystalline solid exploded spontaneously.

See other GOLD COMPOUNDS

See related ORGANOMETALLIC NITRATES

2554. Triethylborane

[97-94-9] **$C_6H_{15}B$**



HCS 1980, 931

1. Meerwein, H., *J. Prakt. Chem.*, 1937, **147**, 240
2. Hideki, Y. *et al., Bull. Chem. Soc. Jap.*, 2001, **74**(2), 225

It ignites on exposure to air [1]. This has been rediscovered when using ethanol solutions [2]

Halogens, or Oxygen

Coates, 1960, 84

It ignites in contact with chlorine or bromine, and explodes in oxygen.

Triethylaluminium

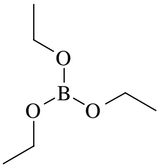
Hurd. D. T., *J. Amer. Chem. Soc.*, 1948, **70**, 2053

Mixtures with triethylaluminium have been used as hypergolic igniters in rocket propulsion systems.

See other ALKYLBORANES

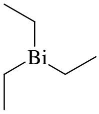
†2555. Triethyl borate

[150-46-9] **$C_6H_{15}BO_3$**



2556. Triethylbismuth

[617-77-6] **$C_6H_{15}Bi$**



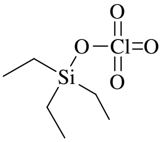
Coates, 1967, Vol. 1, 537

It ignites in air, and explodes at about 150°C, before distillation begins.

See other TRIALKYLBISMUTHS

2557. Triethylsilyl perchlorate

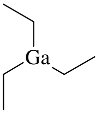
[18244-91-2] **$C_6H_{15}ClO_4Si$**



1. Wannagat, U. *et al., Z. Anorg. Chem.*, 1950, **302**, 185—198
2. Barton, T. J. *et al., J. Org. Chem.*, 1978, **43**, 3651

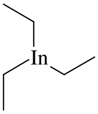
Several trialkyl- or triaryl-silyl perchlorates explode on heating [1]. A syringe used to inject a sample of the title perchlorate ester into a reaction flask exploded soon after addition was complete [2].
See other ORGANOSILYL PERCHLORATES

2558. Triethylgallium
[1115-99-7] **$C_6H_{15}Ga$**



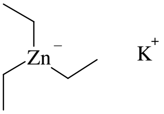
Air, or Water
Dennis, L. M. *et al., J. Amer. Chem. Soc.*, 1932, **54**, 182
The compound ignites in air. Breaking a bulb containing 0.2 g under cold water shattered the container. The monoetherate behaved similarly under 6M nitric acid
See other ALKYLMETALS

2559a. Triethylindium
[923-34-2] **$C_6H_{15}In$**



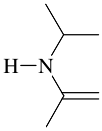
Leleu, *Cahiers*, 1977, (88), 367
It ignites in air.
See other ALKYLMETALS

2559b. Potassium triethylzincate
[92476-41-0] **$C_6H_{15}KZn$**



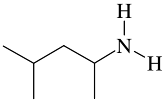
Musswer, C. A. *et al., J. Org. Chem.*, 2000, **65**(23), 7750
A black crystallisable material of the above formula, but not necessarily the structure shown above, is obtainable by mixing the alkylmetals. Recrystallised samples twice decomposed violently.

†2561. Diisopropylamine
[108-18-9] **$C_6H_{15}N$**



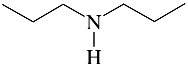
See other ORGANIC BASES

†2562. 1,3-Dimethylbutylamine
[108-09-8] **$C_6H_{15}N$**



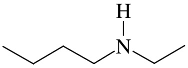
See other ORGANIC BASES

†2563a. Dipropylamine
[142-84-7] **$C_6H_{15}N$**



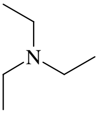
See other ORGANIC BASES

†2563b. *N*-Ethylbutylamine (Butylethylamine)
[13360-63-9] **$C_6H_{15}N$**



See other ORGANIC BASES

†2564. Triethylamine
[121-44-8] **$C_6H_{15}N$**



FPA H92, 1980; *HCS 1980*, 930; *RSC Lab. Hazard Data Sheet No. 27*, 1984

2-Bromo-2,5,5-trimethylcyclopentanone, Potassium hydroxide
See 2-Bromo-2,5,5-trimethylcyclopentanone: Potassium hydroxide, etc.

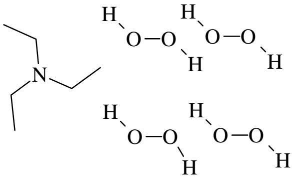
Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Triethylamine

Maleic anhydride
See Maleic anhydride: Bases, etc.

Other reactants
Yoshida, 1980, 247
MRH Values calculated for 13 combinations with oxidants are given.
See other ORGANIC BASES

2565. Triethylamine hydrogen peroxidate

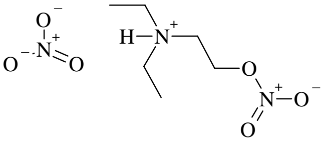
[ ] **$C_6H_{15}N.4H_2O_2$**



See entry CRYSTALLINE HYDROGEN PEROXIDATES

2566. 2-Diethylammonioethyl nitrate nitrate

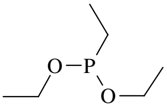
[ ] **$C_6H_{15}N_3O_6$**



1. Barbière, J., *Bull. Soc. Chim. Fr.*, 1944, **11**, 470—480
2. Fakstorp, J. *et al., Acta Chem. Scand.*, 1951, **5**, 968—969

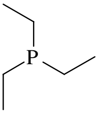
Repetition of the original preparation [1] involving interaction of diethylaminoethanol with fuming nitric acid, followed by vacuum distillation of excess acid, invariably caused explosions during this operation. A modified procedure without evaporation is described [2].
See related ALKYL NITRATES, OXOSALTS OF NITROGENOUS BASES

2567. Diethyl ethanephosphonite
[2651-85-6] **$C_6H_{15}O_2P$**



Arbuzov, B. A. *et al., Chem. Abs.*, 1953, **47**, 3226a
Absorbed on to filter paper it ignites in air.
See other PHOSPHORUS ESTERS
See related ALKYLPHOSPHINES

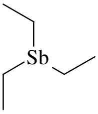
2568. Triethylphosphine
[554-70-1] **$C_6H_{15}P$**



Oxygen
Engler, C. *et al., Ber.*, 1901, **34**, 365
Action of oxygen at low temperature on the phosphine produces an explosive product.

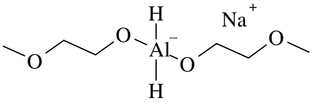
Palladium(II) perchlorate
See Perchloratotris(triethylphosphine)palladium(II) perchlorate
See other ALKYLPHOSPHINES

2569. Triethylantimony
[617-85-6] **$C_6H_{15}Sb$**



von Schwartz, 1918, 322
It ignites in air.
See other ALKYLMETALS

2570. Sodium dihydrobis(2-methoxyethoxy)aluminate
[22722-98-1] **$C_6H_{16}AlNaO_4$**



Preparative hazard

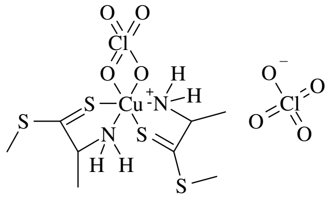
1. Casensky, B. *et al., Inorg. Synth.*, 1978, **18**, 150
2. Strauf, O. *et al., J. Organomet. Chem. Library 15*, 1985
3. Wakakura, M. *et al., J. Loss Prev. Process Ind.*, 1999, **12**, 79
4. Yanagida, S. *et al., Anzen Kogaku*, 1998, **37**(1) 61

The preparation is effected by heating sodium, aluminium powder and 2-methoxyethanol in toluene at 150°C under 70bar pressure of hydrogen in an autoclave. The reaction is exothermic, and hydrogen is first evolved by the dissolving metals, initially increasing the pressure, before absorption of hydrogen into the complex hydride occurs to reduce the pressure. Care in controlling temperature and the volume of reagents charged to the autoclave is necessary to avoid hazards. The solid complex hydride is not pyrophoric with air or water, but concentrated solutions (above 70%) may ignite when exposed to air on dry textiles [1]. It is, however a novel and versatile reducing agent which can with advantage (including that of increased safety in use) replace other complex hydrides [2]. An account is given of an explosion and fire destroying a reactor used for making this. It had previously been employed to make sodium tetrahydroaluminate, a coating of which was left [3]. Although this will, in principle, form the desired product it will react with methoxyethanol very much faster than do the metals, while producing hydrogen as permanent byproduct. This violent kick-start seems to have taken the reaction beyond control [Editor's interpretation]. What may be the same incident, though the not very intelligible English abstract claims the solvent was THF, is reported [4].

See other COMPLEX HYDRIDES, GAS EVOLUTION INCIDENTS

2571. Bis(methyl 1-methylhydrazinocarbodithioate *N*^{2},*S'*)(perchlorato-*O,O'*)copper-(1+) perchlorate

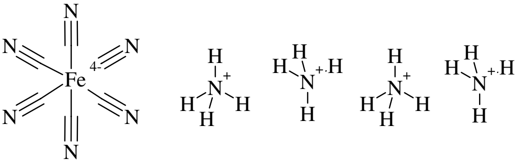
[67870-97-7] **$C_6H_{16}Cl_2CuN_4O_8S_4$**



See Bis-*O,N*[(*N'*-pent-2-en-2-oxy-4-ylidene)-*N,S*-dimethyldithiocarbazate]copper(II) perchlorate

2572. Ammonium hexacyanoferrate(II)

[14481-29-9] **$C_6H_{16}FeN_{10}$**



Hydrochloric acid

Ephraim, 1939, 303

Contact with acids liberates the solid complex ferrocyanic acid which is endothermic (ΔH_f° (aq) +534.7 kJ/mol, 2.48 kJ/g), and forms complexes with diethyl ether etc.

Metal nitrates

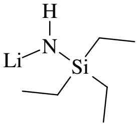
Copper(II) nitrate: Ammonium hexacyanoferrate

See Cobalt(II) nitrate: Ammonium hexacyanoferrate

See related ENDOTHERMIC COMPOUNDS, METAL CYANIDES (AND CYANO COMPLEXES)

2573. Lithium triethylsilylamide

[13270-95-6] **$C_6H_{16}LiNSi$**



Oxidants

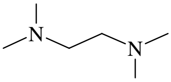
It is hypergolic with fluorine or fuming nitric acid, and explodes with ozone.

See SILYLHYDRAZINES

See other N-METAL DERIVATIVES

†2574. 1,2-Bis(dimethylamino)ethane

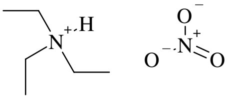
[110-18-9] **$C_6H_{16}N_2$**



See other ORGANIC BASES

2575. Triethylammonium nitrate

[27096-31-7] **$C_6H_{16}N_2O_3$**

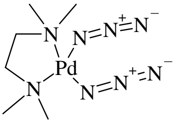


Dinitrogen tetraoxide

See Dinitrogen tetraoxide: Triethylammonium nitrate

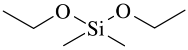
See other OXOSALTS OF NITROGENOUS BASES

2576. Diazido(N,N,N,N-tetramethylethanediamine)palladium
[158668-93-0] **$C_6H_{16}N_8Pd$**



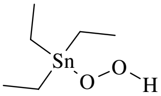
Kim, Y. *et al., Bull. Korean Chem. Soc.*, 1994, **15**(8), 690
Exploded during melting point determination.
See AZIDES

†2577. Diethoxydimethylsilane
[78-62-6] **$C_6H_{16}O_2Si$**



See related ALKYLSILANES

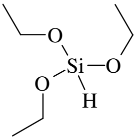
2578. Triethyltin hydroperoxide (Triethylstannyl hydroperoxide)
[44797-71-9] **$C_6H_{16}O_2Sn$**



Hydrogen peroxide

Aleksandrov, Y. A. *et al., Zh. Obsch. Khim.*, 1965, **35**, 115
While the hydroperoxide is stable at ambient temperature, the addition compound which it readily forms with excess hydrogen peroxide is not, decomposing violently.
See other ORGANOMETALLIC PEROXIDES

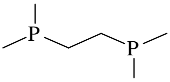
2580. Triethoxysilane
[998-30-1] **$C_6H_{16}O_3Si$**



1. Xin, S. *et al., Can. J. Chem.*, 1990, **68**, 471
2. Buchwald, S. L., *Chem. Eng. News*, 1993, **71**(13), 2

This compound can disproportionate, generating silane (SiH_4) which is liable to be pyrophoric. Presumably other alkoxy silanes can do likewise [1]. Its use as a reducing agent for the preparation of alcohols from esters is considered safer in air than under an inert atmosphere, which latter permits accumulation of silane to hazardous levels and later fire or explosion. [2]
See related SILANES

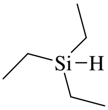
2581a. Ethylenebis(dimethylphosphine)
[23936-60-9] **$C_6H_{16}P_2$**



1. Burt, R. J., *J. Organomet. Chem.*, 1979, **182**, 205
2. Butter, S. A. *et al., Inorg. Synth.*, 1974, **15**, 190

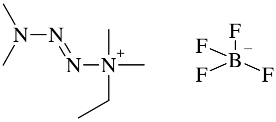
Though air sensitive [1], it is not pyrophoric as reported previously [2].
See other ALKYLPHOSPHINES

2581b. Triethylsilane
[617-86-7] **$C_6H_{16}Si$**



Boron trichloride
See Boron trichloride: Triethylsilane
See other ALKYLSILANES

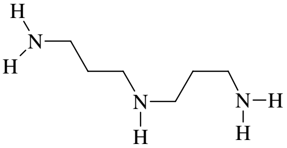
2582. 1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate
[65651-91-4] **$C_6H_{17}BF_4N_4$**



Stöldt, E. *et al., Angew. Chem. (Intern,. Ed.)*, 1978, **17**, 203
An explosive salt.
See other PERCHLORATE SALTS OF NITROGENOUS BASES, TETRAZENES

2583a. 3,3′-Iminobispropylamine (Norspermidine)

[56-18-8] **$C_6H_{17}N_3$**



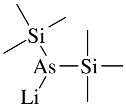
Editor's comments, 1993

Various secondary sources of safety data are now listing this as an explosive. I can find no primary source for this classification, which seems very improbable. Simple minded use of many computational hazard prediction procedures would show thermodynamically that this compound, like most lower amines, could hypothetically convert to alkane, ammonia and nitrogen with sufficient energy (about 3 kJ/g) to count as an explosion hazard. This reaction is not known to happen. (Simple minded thermodynamicists would rate this book, or computer, and its reader as a severe hazard in an air environment.) Like other bases, iminobispropylamine certainly sensitises many nitro-explosives to detonation. It is used experimentally to study the effect, which may have found technical exploitation and, garbled, could have led to description of the amine as itself an explosive.

See COMPUTATION OF REACTIVE CHEMICAL HAZARDS, C—NITRO COMPOUNDS

2583b. Lithium bis(trimethylsilyl)arsenide

[76938-15-3] **$C_6H_{18}AsLiSi_2$**



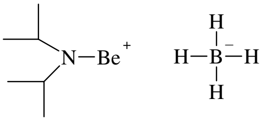
Wills, R. *et al., Inorg. Synth.*, 1997, **31**, 150

Pyrophoric.

See related ALKYLSILANES

2583c. Diisopropylaminoberylium tetrahydroborate (Beryllium diisopropylamide borohydride)

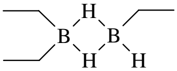
[ ] **$C_6H_{18}BBeN$**



Näth, H. *et al., Eur. J. Inorg. Chem.*, 2003, (12), 2245

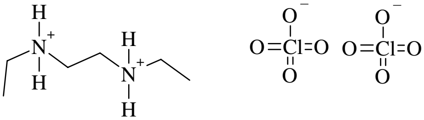
This compound, which exists as a dimer with tricordinate beryllium, demonstrates explosive combustion.

2584. Triethyldiborane
[62133-36-2] $C_6H_{18}B_2$



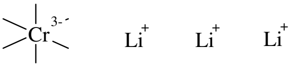
Leleu, *Cahiers*, 1977, (88), 365
It ignites in air.
See other ALKYLBORANES

2585. 1,2-Bis(ethylammonio)ethane perchlorate
[53213-78-8] $C_6H_{18}Cl_2N_2O_8$



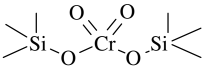
Sunderlin, K. G. R., *Chem. Eng. News*, 1974, **52**(31), 3
It exploded mildly under an impact of 11.5 kgm.
See other PERCHLORATE SALTS OF NITROGENOUS BASES

2586. Lithium hexamethylchromate(3—)
[14931-97-6] (tris-dioxane complex) $C_6H_{18}CrLi_3$



Kurras, E. *et al., J. Organomet. Chem.*, 1965, **4**, 114—118
Isolated as a dioxane complex, it ignites in air.
See related ALKYLMETALS

2587. Bis(trimethylsilyl) chromate
[1746-09-4] $C_6H_{18}CrO_4Si$

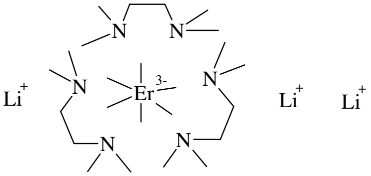


1. Anon., *ABCM Quart. Safety Summ.*, 1960, **31**, 16
2. Schmidt, M. *et al., Angew. Chem.*, 1958, **70**, 704

Small quantities can be distilled at about 75°C/1.3 mbar, but larger amounts are liable to explode violently owing to local overheating [1]. An attempt to prepare an analogous poly(dimethylsilyl) chromate by heating a polydimethylsiloxane with chromium trioxide at 140°C exploded violently after 20 min at this temperature [2].
See related ALKYLSILANES, METAL OXIDES

2588. Hexamethylerbium—hexamethylethylenediaminelithium complex

[66862-11-1] **$C_6H_{18}Er.3C_2H_{16}N_2Li$**



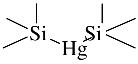
Schumann, H. *et al., Angew. Chem. (Intern. Ed.)*, 1981, **20**, 120—121

It ignites in air, as do the analogous derivatives of lutetium and other lanthanoids

See related ALKYLMETALS

2589. Bis(trimethylsilyl)mercury

[4656-04-6] **$C_6H_{18}HgSi_2$**



Eisch, J. J. *et al., J. Organomet. Chem.*, 1979, **171**, 149

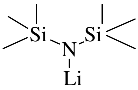
Momentary exposure of traces of the product on a stopper to air usually causes ignition.

See other MERCURY COMPOUNDS

See related ALKYLSILANES

2590. Lithium bis(trimethylsilyl)amide

[4039-32-1] **$C_6H_{18}LiNSi_2$**



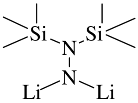
Amonoo-Neizer, E. H. *et al., Inorg. Synth.*, 1966, **8**, 21

It is unstable in air and ignites when compressed.

See other N-METAL DERIVATIVES

2591. Dilithium 1,1-bis(trimethylsilyl)hydrazide

[15114-92-8] **$C_6H_{18}Li_2N_2Si_2$**



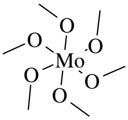
It ignites in air.

See entry SILYLHYDRAZINES

See other N-METAL DERIVATIVES, METAL HYDRAZIDES

2592. Molybdenum hexamethoxide

[135840-44-7] **$C_6H_{18}MoO_6$**



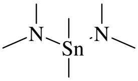
Preparative hazard

See Tetramethoxysilane: Metal hexafluorides

See other METAL ALKOXIDES

2593. Bis(dimethylamino)dimethylstannane

[993-74-8] **$C_6H_{18}N_2Sn$**



Chloroform

Randall, E. W. *et al., Inorg. Nucl. Chem. Lett.*, 1965, **1**, 105

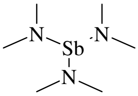
Gentle heating of a 1:1 chloroform solution of the stannane led to a mild explosion. Similar explosions had been experienced at the conclusion of fractional distillation of other bis(dialkylamino)stannanes where the still pot temperature had risen to about 200°C.

See other N-METAL DERIVATIVES

See related ALKYLMETALS

2594. Tris(dimethylamino)antimony

[7289-92-1] **$C_6H_{18}N_3Sb$**



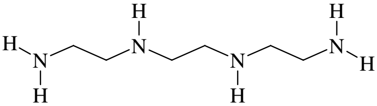
Ethyl diazoacetate

See Ethyl diazoacetate: Tris(dimethylamino)antimony

See other N-METAL DERIVATIVES

2595. *N,N′*-Bis(2-aminoethyl)1,2-diaminoethane (Triethylenetetramine)

[112-24-3] **$C_6H_{18}N_4$**



Cellulose nitrate

See CELLULOSE NITRATE: AMINES

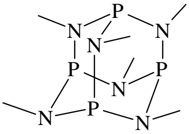
Other reactants

Yoshida, 1980, 251

MRH values calculated for 13 combinations with oxidants are given.

See other ORGANIC BASES

2596. 2,4,6,8,9,10-Hexamethylhexaaza-1,3,5,7-tetraphosphaadamantane
[10369-17-2] **$C_6H_{18}N_6P_4$**



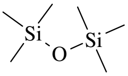
Oxidants

Verdier, F., *Rech. Aerosp.*, 1970, (137), 181—189

Among other solid P—N compounds examined, the title compound ignited immediately on contact with nitric acid, hydrogen peroxide or dinitrogen trioxide.

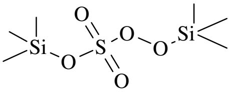
See ROCKET PROPELLANTS

†2597. Bis(trimethylsilyl) oxide
[107-46-0] **$C_6H_{18}OSi_2$**



See related ALKYLSILANES

2598. Bis(trimethylsilyl) peroxomonosulfate
[23115-33-5] **$C_6H_{18}O_5SSi_2$**



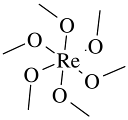
Blaschette, A. *et al., Angew. Chem. (Intern. Ed.)*, 1969, **8**, 450

It is stable at —30°C, but on warming to ambient temperature it decomposes violently evolving sulfur trioxide.

See other GAS EVOLUTION INCIDENTS, PEROXYESTERS, SULFUR ESTERS

2599. Rhenium hexamethoxide

[ ] **$C_6H_{18}O_6Re$**



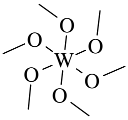
Preparative hazard

See Tetramethoxysilane: Metal hexafluorides

See other METAL ALKOXIDES

2600. Tungsten hexamethoxide

[35869-33-1] **$C_6H_{18}O_6W$**



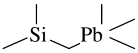
Preparative hazard

See Tetramethoxysilane: Metal hexafluorides

See other METAL ALKOXIDES

2601. (Dimethylsilylmethyl)trimethyllead

[ ] **$C_6H_{18}PbSi$**



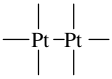
Schmidbaur, H., *Chem. Ber.*, 1964, **97**, 270

It decomposes slowly above 100°C, and with explosive violence in presence of oxygen.

See related ALKYLMETALS, ALKYLSILANES

2602. Hexamethyldiplatinum

[4711-74-4] **$C_6H_{18}Pt_2$**



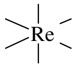
Gilman, H. *et al., J. Amer. Chem. Soc.*, 1953, **75**, 2065

It explodes sharply in a shower of sparks on heating.

See other ALKYLMETALS, PLATINUM COMPOUNDS

2603. Hexamethylrhenium

[56090-02-9] **$C_6H_{18}Re$**



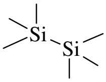
1. Mertis, K. *et al., J. Organomet. Chem.*, 1975, **97**, C65
2. Mertis, K. *et al., J. Chem. Soc., Dalton Trans.*, 1976, 1489
3. Edwards, P. G. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 2474

It should be handled with extreme caution, even in absence of air, because dangerous explosions have occurred on warming frozen samples, or during transfer operations [1]. It is unstable above —20°C, and on one occasion admission of nitrogen to the solid under vacuum caused a violent explosion [2]. It should be prepared only as required and in small amounts, and in use, oxygen and moisture must be rigorously excluded [3].

See other ALKYLMETALS

2604. Hexamethyldisilane

[1450-14-2] **$C_6H_{18}Si_2$**



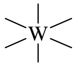
Pyridine *N*-oxide, Tetrabutylammonium fluoride

See Pyridine *N*-oxide: Hexamethyldisilane, Tetrabutylammonium fluoride

See other ALKYLSILANES

2605. Hexamethyltungsten

[36133-73-0] **$C_6H_{18}W$**



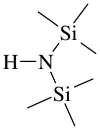
Galyer, L. *et al., J. Organomet. Chem.*, 1975, **85**, C37

Several unexplained and violent explosions during preparation and handling indicate that the compound must be handled with great care and as potentially explosive, particularly during vacuum sublimation.

See other ALKYLMETALS

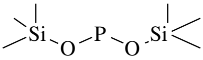
†2606. Hexamethyldisilazane

[999-97-3] **$C_6H_{19}NSi_2$**



See related ALKYLSILANES

2607. Bis(trimethylsilyl) phosphonite (Bis(trimethylsilyloxy)phosphine)
[30148-50-6] **$C_6H_{19}O_2PSi_2$**

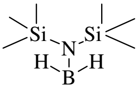


1. Hata, T. *et al., Chem. Lett.*, 1977, 1432
2. Montchamp, J-L. *et al., J. Org. Chem.*, 1995, **60**(19), 6076

It ignites in air [1]. A means of preparing and using this reagent in situ is described [2].

See other PHOSPHORUS ESTERS, PYROPHORIC MATERIALS

2608. *N,N*-Bis(trimethylsilyl)aminoborane
[73452-31-0] **$C_6H_{20}BNSi_2$**

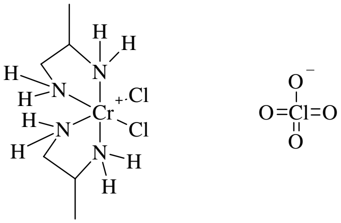


Wisian-Nielsen, P., *J. Inorg. Nucl. Chem.*, 1979, **41**, 1546

It ignites in direct contact with air.

See related ALKYLSILANES, BORANES

2609. Bis(1,2-diaminopropane)-*cis*-dichlorochromium(III) perchlorate
[59598-02-6] **$C_6H_{20}Cl_3CrN_4O_4$**



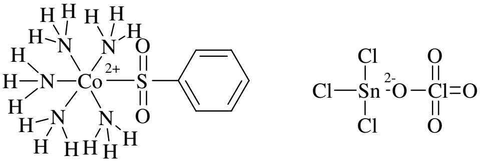
Perchloric acid

Anon., *Chem. Eng. News*, 1963, **41**(27), 47

A mixture of the complex and 20 volumes of 70% acid was being stirred at 22°C when it exploded violently. Traces of ether or ethanol may have been present. Extreme care must be exercised when concentrated perchloric acid is contacted with organic materials with agitation or without cooling.

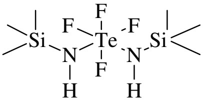
See other AMMINEMETAL OXOSALTS

2610. (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II)
[64825-48-5] **$C_6H_{20}Cl_4CoN_5O_6SSn$**



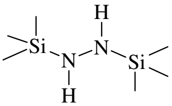
Elder, R. C. *et al., Inorg. Chem.*, 1978, **17**, 427
It explodes at temperatures around 150°C. Thermal decomposition appears to involve an internal redox reaction in the anion leading to formation of trichloro(chlorato)oxostannate(IV).
See other AMMINEMETAL OXOSALTS, REDOX COMPOUNDS
See related METAL PERCHLORATES, REDOX REACTIONS

2611. *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride
[86045-52-5] **$C_6H_{20}F_4N_2Si_2Te$**



Hartl, H. *et al., Inorg. Chem.*, 1983, **22**, 2183—2184
The colourless solid explodes mildly at 100°C, but a 50 g sample on keeping for 6 months in a stoppered cylinder was converted to a yellow extremely explosive solid, probably a hydrolysis product.
See other AMMINEMETAL HALIDES
See related ALKYLSILANES, METAL HALIDES

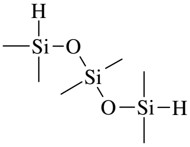
2612. 1,2-Bis(trimethylsilyl)hydrazine
[692-56-8] **$C_6H_{20}N_2Si_2$**



Oxidants
It is hypergolic with fluorine or fuming sulfuric acid.
See entry SILYLHYDRAZINES

2613a. Hexamethyltrisiloxane

[1189-93-1] **$C_6H_{20}O_2SI_3$**

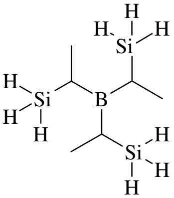


See entry SILANES; Olefins, Platinum

See related ALKYLSILANES

2613b. Tris(1-silylethyl)borane

[256453-50-6] **$C_6H_{21}BSi_3$**



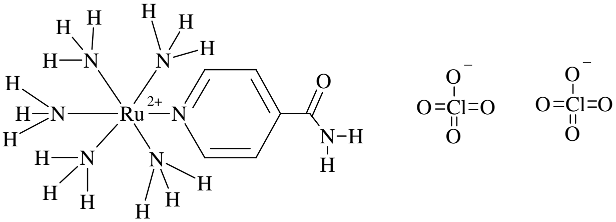
Weinmann, M. *et al., J. Organomet. Chem.*, 1999, **592**(1), 115

This compound, and the homologues with one or two methyl groups on the silyl moiety, explodes on exposure to air, and is moisture sensitive.

See other ALKYLBORANES, SILANES

2614. Isonicotinamidepentaammineruthenium(II) perchlorate

[31279-70-6] **$C_6H_{21}Cl_2N_7O_9Ru$**



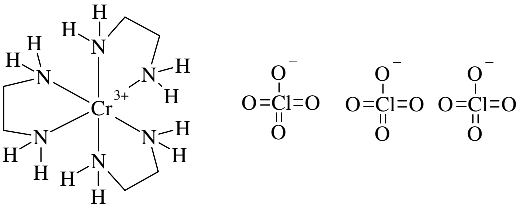
Stanbury, D.M. *et al., Inorg Chem.*, 1980, **19**, 519

It is explosive.

See other AMMINEMETAL OXOSALTS

2615. Tris(1,2-diaminoethane)chromium(III) perchlorate

[15246-55-6] **$C_6H_{24}Cl_3CrN_6O_{12}$**



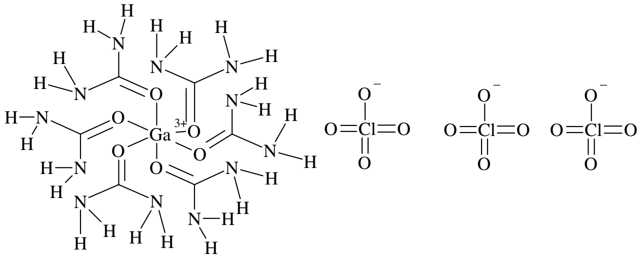
Olander, D. E., *Chem. Eng. News*, 1984, **62**(10), 2, 39

It is a treacherously sensitive, very brisant primary explosive (while its cobalt analogue is a well behaved secondary explosive).

See other AMMINEMETAL OXOSALTS

2616. Hexaureagallium(III) perchlorate

[31332-72-6] **$C_6H_{24}Cl_3GaN_{12}O_{18}$**



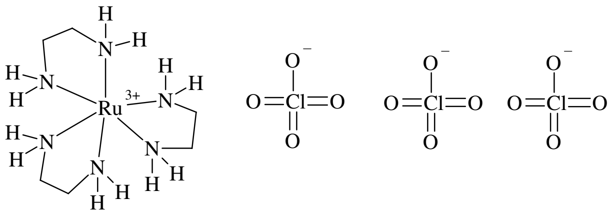
Lloyd, D. J. *et al., J. Chem. Soc.*, 1943, 76

It decomposes violently when heated above its m.p., 179°C.

See related AMMINEMETAL OXOSALTS

2617. Tris(1,2-diaminoethane)ruthenium(III) perchlorate

[67187-50-2] **$C_6H_{24}Cl_3N_6O_{12}Ru$**

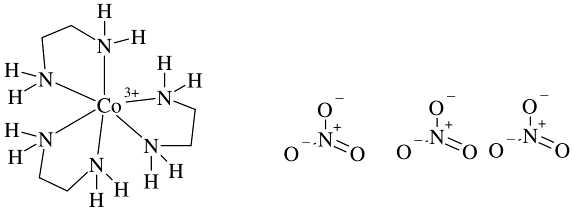


Lavallee, U. *et al., Inorg. Chem.*, 1978, **17**, 2218

An attempt to prepare the perchlorate salt led to an explosion.

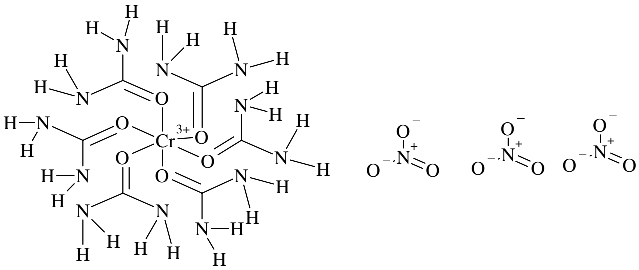
See other AMMINEMETAL OXOSALTS

2618. Tris(1,2-diaminoethane)cobalt(III) nitrate
[6865-68-5] **$C_6H_{24}CoN_9O_9$**



Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 375
No explosion on heating, but medium impact-sensitivity.
See other AMMINEMETAL NITRATES

2619. Hexaureachromium(III) nitrate
[22471-42-7] **$C_6H_{24}CrN_{15}O_{15}$**



Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 375
Explodes at 265°C, medium impact-sensitivity.
See related AMMINEMETAL NITRATES

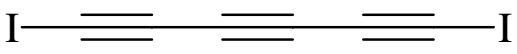
2620a. 1,1′-Azo-[2-methyl-1,2-dicarbadodecaborane(14)]
[73469-45-1] **$C_6H_{26}B_{20}N_2$**

[1975]

Preparative hazard
Totari, T. *et al., J. Chem. Soc., Chem. Commun.*, 1979, 1051
The reaction mixture from permanganate oxidation of the aminocarbaborane in liquid ammonia must be diluted with toluene at —60°C to avoid detonation when the ammonia is subsequently evaporated.
See AZOCARBABORANES
See related BORANES

2620b. Diiodohexatriyne

[301831-66-3] **C_6I_2**



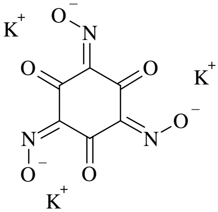
Gao, K. *et al., J. Amer. Chem. Soc.*, 2000, **122**(38), 9320

Explodes above 100 C during melting point determination.

See other HALOACETYLENE DERIVATIVES

2621. Potassium cyclohexanehexone 1,3,5-trioximate

[ ] **$C_6K_3N_3O_6$**



Alone, or Acids

Benedikt, R., *Ber.*, 1878, **11**, 1375

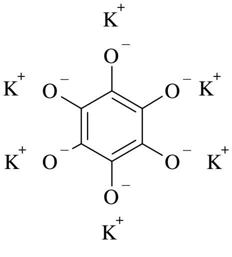
The salt explodes on heating above 130°C or if moistened with sulfuric or nitric acids. The lead salt also explodes violently on heating.

See other N—O COMPOUNDS

See related OXIMES

2622. Potassium benzenehexoxide

[3264-86-6] **$C_6K_6O_6$**



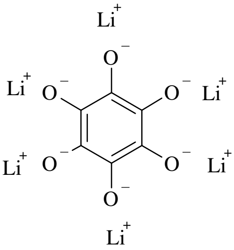
Air, or Oxygen, or Water

1. Sorbe, 1968, 68, 69
2. Mellor, 1963, Vol. 2, Suppl. 2.2, 1567—1568; 1946, Vol. 5, 951
3. Weiss, E., *Angew. Chem. (Int.)*, 1993, **32**(11), 1518

The compound ‘potassium carbonyl’ is now thought to be the hexameric potassium salt of hexahydroxybenzene, and reacts with moist air to give a very explosive product [1]. It reacts violently with oxygen, and explodes on heating in air or in contact with water [2]. There are probably two compounds described, the original preparation from

carbon monoxide and liquid potassium may well give the aromatic structure. X-ray crystallography shows the product from potassium and carbon monoxide in liquid ammonia to be dipotassium ethynediolate [3].
See Potassium: Non-metal oxides (reference 4)

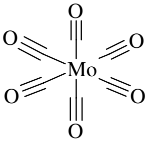
2623. Lithium benzenehexoxide
[101672-16-6] **$C_6Li_6O_6$**



Water
1. Mellor, 1961, Vol. 2, Suppl. 2.1, 88
2. Weiss, E., *Angew. Chem. (Int.)*, 1993, **32**(11), 1518

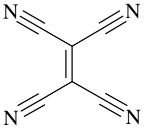
Like the potassium compound, it explodes with water [1]. It is probable that this compound is actually dilithium ethynediolate [2].

2624. Hexacarbonylmolybdenum
[13939-06-5] **C_6MoO_6**



Diethyl ether
Owen, B. B. *et al., Inorg. Synth.*, 1950, **3**, 158
Solutions of hexacarbonylmolybdenum in ether have exploded after extended storage.
See other CARBONYLMETALS

2625. Tetracyanoethylene
[670-54-2] **C_6N_4**



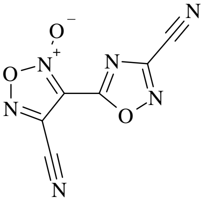
1-Methylsilacyclopenta-2,4-diene

See 1-Methylsilacyclopenta-2,4-diene: Dienophiles

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS

2626. 3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2-(or 5-) oxide

[56092-91-2] **$C_6N_6O_3$**



Hydrazine derivatives

Lupton, E. C. *et al., J. Chem. Eng. Data*, 1975, **20**, 136

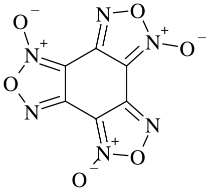
The compound is highly endothermic (ΔH_f° (s) +565.5 kJ/mol, 2.77 kJ/g), and interaction with hydrazines is explosive.

See Dicyanofurazan: Nitrogenous bases

See other CYANO COMPOUNDS, ENDOTHERMIC COMPOUNDS, FURAZAN N-OXIDES

2627. Benzotri(furazan *N*-oxide) (Hexanitrosobenzene)

[3470-17-5] **$C_6N_6O_6$**



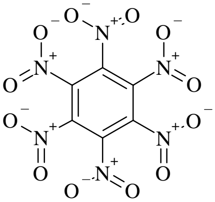
1. Selig, W., *Z. Anal. Chem.*, 1978, **289**, 44—46
2. McGuire, R. R., *Chem. Abs.*, 1978, **89**, 131857
3. *CHETAH*, 1990, 182

It is explosive [1], and the limited thermal stability is reduced by traces of triazidotrinitrobenzene as impurity [2]. It is shock sensitive [3].

See other FURAZAN N-OXIDES

2628. Hexanitrobenzene

[13232-74-1] **$C_6N_6O_{12}$**



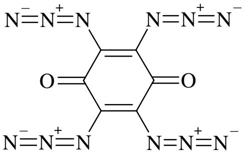
Nielsen, A. T. *et al., J. Org. Chem.*, 1979, **44**, 1181

The compound (of zero oxygen balance) is a powerful explosive, as is pentanitrobenzene. As a nitrocarbon, it has similar properties to tetranitromethane and hexanitroethane.

See other POLYNITROARYL COMPOUNDS

2629a. Tetraazido-1,4-benzoquinone

[22826-61-5] **$C_6N_{12}O_2$**



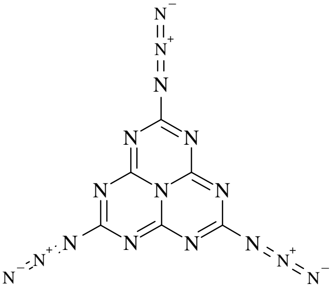
1. Friess, K. *et al., Ber.*, 1923, **56**, 1304
2. Gilligan, W. H. *et al., Tetrahedron Lett.*, 1978, 1675—1676
3. Winkelmann, E., *Tetrahedron*, 1969, **25**, 2427

Extremely explosive, sensitive to heat, friction and impact. A single crystal heated on a spatula exploded and bent it badly [1]. It explodes at 120°C, and the impact-sensitivity was too high to be measured, extreme friction sensitivity causing explosions when samples were being arranged on sandpaper. Quantities above 100—200 mg are too dangerous to prepare and handle under ordinary laboratory conditions [2], the 24 g scale previously described [3] being dangerously excessive.

See other 2-AZIDOCARBONYL COMPOUNDS, HIGH-NITROGEN COMPOUNDS

2629b. Triazido-*sym*-heptazine

[ ] **C_6N_{16}**



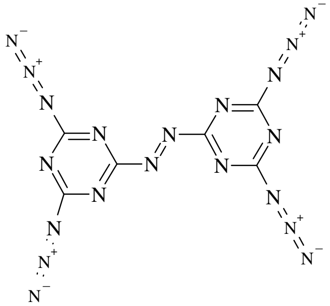
Miller, D. R. *et al., J. Amer. Chem. Soc.*, 2004, **126**(17), 5372

Surprisingly stable for a polyazide of such high nitrogen content, the authors ground the material in a glazed mortar – though it showed signs of decomposition in an unglazed porcelain one. However they describe it as having the sensitivity of a primary explosive. It decomposes vigorously at 185°C to a residue approximating to carbon nitride, C_3N_4.

See other HIGH-NITROGEN COMPOUNDS

2629c. Azobis(2,6-diazido-1,2,5-triazine)

[771577-80-1] **C_6N_{20}**



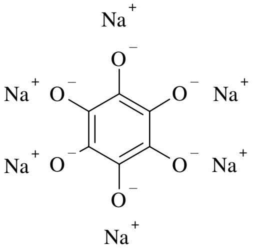
Huynh, M. H. V., *et al., Angew. Chem. (Int.)*, 2004, **43**(37), 4924

Claimed to have the highest known molar ΔH_f°, $+ 2171$ kJ/mole $= 6.15$ kJ/g, it is, of course, a sensitive explosive

See other HIGH-NITROGEN COMPOUNDS

2630. Sodium benzenehexoxide

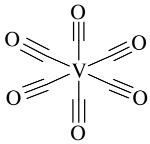
[101672-22-4] **$C_6Na_6O_6$**



See Sodium: Non-metal oxides (reference 4)

2631. Hexacarbonylvanadium

[14024-00-1] **C_6O_6V**

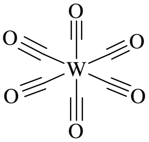


1. Pruett, R. L. *et al., Chem. & Ind.*, 1960, 119
2. Bailar, 1973, Vol. 3, 529

The pyrophoric compound previously regarded as ‘dodecacarbonyl divanadium’ [1] is now known to be the monomeric hexacarbonylvanadium [2].

See other CARBONYLMETALS

2632. Hexacarbonyltungsten
[14040-11-0] **C_6O_6W**



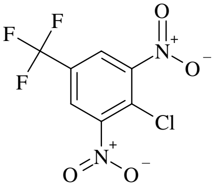
Preparative hazard

Hurd, D. T. *et al., Inorg. Chem.*, 1957, **5**, 136

It is dangerous to attempt the preparation from tungsten hexachloride, aluminium powder and carbon monoxide in an autoclave of greater than 0.3 l capacity.

See other CARBONYLMETALS

2633. 2-Chloro-1,3-dinitro-5-trifluoromethylbenzene
[393-75-9] **$C_7H_2ClF_3N_2O_4$**

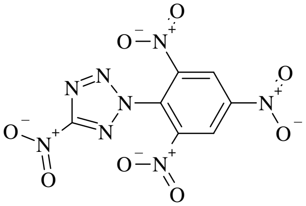


Nazarov, V. P. *et al., Chem. Abs.*, 1980, **93**, 2387

Mathematical modelling was used to develop the recommendation to use a cascade of 3 reactors for the highly exothermic dinitration of 4-chloro-trifluoromethylbenzene.

See other NITRATION INCIDENTS, POLYNITROARYL COMPOUNDS

2634. 5-Nitro-2-picryltetrazole
[82177-75-1] **$C_7H_2N_8O_8$**



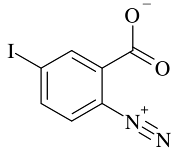
Spear, R. J. *et al., Chem. Abs.*, 1983, **98**, 91969

Powerfully explosive but of low impact-sensitivity.

See other POLYNITROARYL COMPOUNDS, TETRAZOLES

2635. 4-Iodobenzenediazonium-2-carboxylate

[ ] **$C_7H_3IN_2O_2$**



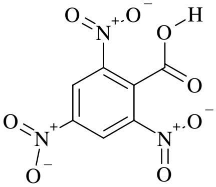
Gommper, R. *et al., Chem. Ber.*, 1968, **101**, 2348

It is a highly explosive solid.

See other DIAZONIUM CARBOXYLATES

2636. 2,4,6-Trinitrobenzoic acid

[129-66-8] **$C_7H_3N_3O_8$**



an explosive somewhat more sensitive and less powerful than its progenitor, TNT.

Heavy metals

Kranz, A. *et al., Chem. Age* (London), 1925, **13**, 392

All heavy metal salts prepared were explosive on heating or impact.

See other POLYNITROARYL COMPOUNDS

Preparative hazard

See Sodium dichromate: Sulfuric acid, Trinitrotoluene

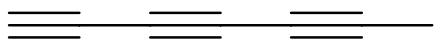
Water vapour

Köhler, J. Meyer, R. Explosives, Weineim, VCH, 1993

On prolonged exposure it slowly decarboxylates to the slightly more sensitive and more powerful trinitrobenzene.

2637. Hepta-1,3,5-triyne

[66486-68-8] **C_7H_4**



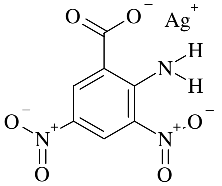
Cook, C. L. *et al., J. Chem. Soc.*, 1952, 2890

It explodes very readily (in absence of air) above 0°C, and the distillation residues also exploded on admission of air.

See other ALKYNES

2638. Silver 3,5-dinitroanthranilate

[58302-42-4] **$C_7H_4AgN_3O_6$**



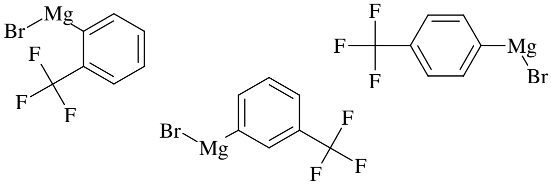
Gupta, S. P. *et al., Def. Sci. J.*, 1975, **25**, 101—106

It explodes at 394°, and the copper salt at 371°C, each after a 10 s delay. They are not impact-sensitive.

See other POLYNITROARYL COMPOUNDS, SILVER COMPOUNDS

2639. 2-, 3- or 4-Trifluoromethylphenylmagnesium bromide

[395-47-1, 402-26-6, 402-51-7, resp.] **$C_7H_4BrF_3Mg$**



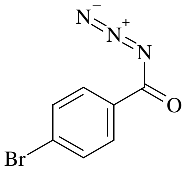
1. Appleby, J. C., *Chem. & Ind.*, 1971, 120
2. ‘Benzotrifluorides Catalog 6/15’ West Chester (Pa)., Marshallton Res. Labs., 1971
3. Taylor, R. *et al.*, private comm., 1973
4. Moore, *et al., Chem. Eng. News*, 1997, **75**(11), 6

During a 2 kg preparation under controlled conditions, the 3- isomer exploded violently [1]. The same had occurred previously in a 1.25 kg preparation 30 min after all magnesium had dissolved. A small preparation of the 2- isomer had also exploded. It was found that 3- preparations in ether decomposed violently at 75° and in benzene—THF at 90°C. Molar preparations or less have been done several times uneventfully when temperatures below 40°C were maintained, but caution is urged [2]. The 3- and 4- reagents prepared in ether exploded when the temperature was raised by adding benzene and distilling the ether out [3]. Twentyfive years after the establishment of a hazard, a sample of the 4-isomer, which had been all but isolated by evaporation of ether, exploded; the experimenters sought to blame hypothetical residues of highly active magnesium [4].

See other FLUORINATED ORGANOLITHIUM COMPOUNDS, GRIGNARD REAGENTS, HALO-ARYLMETALS

2640. 4-Bromobenzoyl azide

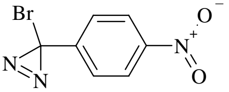
[14917-59-0] **$C_7H_4BrN_3O$**



Curtiss, T. *et al., J. Prakt. Chem.*, 1898, **58**, 201
It explodes violently above its m.p., 46°C.
See other ACYL AZIDES

2641. 3-Bromo-3(4-nitrophenyl)-3*H*-diazirine

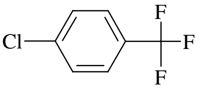
[115127-49-6] **$C_7H_4BrN_3O_2$**



Tetrabutylammonium fluoride
Terpinski, J. *et al., Magn. Reson. Chem.*, 1987, **25**, 924
Direct introduction of the bromodiazirine into molten tetrabutylammonium fluoride (at 63°C) to effect halogen exchange leads to an explosion. Use of acetonitrile at 0°C as solvent gives a low yield of the required fluorodiazirine.
See other DIAZIRINES, N-HALOGEN COMPOUNDS, NITROARYL COMPOUNDS

2642. 4-Chlorotrifluoromethylbenzene

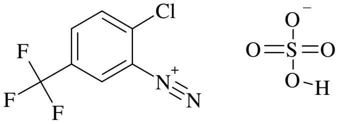
[98-56-6] **$C_7H_4ClF_3$**



Sodium dimethylsulfinate
Meschino, J. A. *et al., J. Org. Chem.*, 1971, **36**, 3637, footnote 9
Interaction with dimethylsulfinate anion (from the sulfoxide and sodium hydride) at —5°C is very exothermic, and addition of the chloro compound must be slow to avoid violent eruption.
See other HALOARYL COMPOUNDS

2643. 2-Chloro-5-trifluoromethylbenzenediazonium hydrogen sulfate

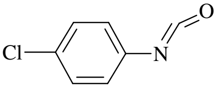
[29362-18-3] (ion) **$C_7H_4ClF_3N_2O_4S$**



See entry DIAZONIUM SULFATES

2644. 4-Chlorophenyl isocyanate

[104-12-1] **C_7H_4ClNO**



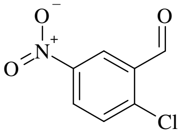
Preparative hazard

See 4-Chlorobenzoyl azide

See other ORGANIC ISOCYANATES

2645. 2-Chloro-5-nitrobenzaldehyde

[6361-21-3] **$C_7H_4ClNO_3$**



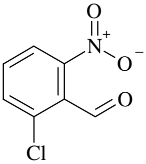
Initial decomposition temperature by ARC was 156°C.

See entry NITROBENZALDEHYDES

See other NITROARYL COMPOUNDS

2646. 2-Chloro-6-nitrobenzaldehyde

[6361-22-4] **$C_7H_4ClNO_3$**



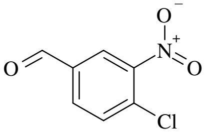
Initial decomposition temperature by ARC was 146°C.

See entry NITROBENZALDEHYDES

See other ALDEHYDES, NITROARYL COMPOUNDS

2647. 4-Chloro-3-nitrobenzaldehyde

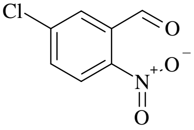
[16588-34-4] **$C_7H_4ClNO_3$**



Initial decomposition temperature by ARC was 116°C.
See entry NITROBENZALDEHYDES
See other ALDEHYDES, NITROARYL COMPOUNDS

2648. 5-Chloro-2-nitrobenzaldehyde

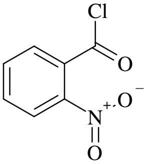
[6628-86-0] **$C_7H_4ClNO_3$**



Initial decomposition temperature by DSC was 240°C.
See entry NITROBENZALDEHYDES
See other ALDEHYDES, NITROARYL COMPOUNDS

2649. 2-Nitrobenzoyl chloride

[610-14-0] **$C_7H_4ClNO_3$**



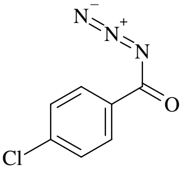
1. Cook, N. C. *et al., Chem. Eng. News*, 1945, **23**, 2394
2. Bonner, W. D. *et al., J. Amer. Chem. Soc., 1946,* **68**, 344; *Chem. & Ind.*, 1948, 89
3. *MCA Case History No. 1915*
4. Lockemann, G. *et al., Ber.*, 1947, **80**, 488
5. *CHETAH*, 1990, 189
6. Lever, S. D. *et al., J. Haz. Mat.*, 2004, **115**(1-3), 91

The hot material remaining after vacuum stripping of solvent up to 130°C decomposed with evolution of gas and then exploded violently 50 min after heating had ceased. Further attempts to distil the acid chloride even in small amounts at below 1.3 mbar caused exothermic decomposition at 110°C. It was, however, possible to flash-distil the chloride in special equipment [1]. Two later similar publications recommend use in solution of the unisolated material [2]. Smaller scale distillation of the chloride at 94—95°C/0.03 mbar had been uneventful, but a 1.2 mol scale preparation exploded during distillation at 128°C/1.2 mbar [3], even in presence of phosphorus pentachloride, previously recommended to reduce the danger of explosion during distillation [4]. Many previous explosions had been reported, and the need for adequate purity of intermediates was stressed. It is shock sensitive [5]. The decomposition reaction has been studied. It depends upon the heating rate and thermal history of the sample, making DSC and similar results difficult to translate into process precautions. Some key features have been identified [6].

See other GAS EVOLUTION INCIDENTS, NITROACYL HALIDES

2650. 4-Chlorobenzoyl azide

[14848-01-2] **$C_7H_4ClN_3O$**



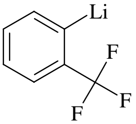
1. Cobern, D. *et al., Chem. & Ind.*, 1965, 1625; 1966, 375
2. Tyabji, M. M., *Chem. & Ind.*, 1965, 2070

A violent explosion occurred during vacuum distillation of 4-chlorophenyl isocyanate, prepared by Curtius reaction from the azide. It was found by IR spectroscopy that this isocyanate (as well as others prepared analogously) contained some unchanged azide, to which the explosion was attributed. The use of IR spectroscopy to check for absence of azides in isocyanates is recommended before distillation [1]. Subsequently, the explosion was attributed to free hydrogen azide, produced by hydrolysis of the unchanged acyl azide [2].

See other ACYL AZIDES

2651. 2-Trifluoromethylphenyllithium

[49571-31-5] **$C_7H_4F_3Li$**



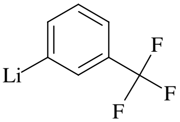
(Preparative hazard for 2-)

See entry ORGANOLITHIUM REAGENTS

See other HALO-ARYLMETALS

2652. 3-Trifluoromethylphenyllithium

[368-49-0] **$C_7H_4F_3Li$**



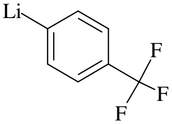
(Preparative hazard for 2-)

See entry ORGANOLITHIUM REAGENTS

See other HALO-ARYLMETALS

2653. 4-Trifluoromethylphenyllithium

[2786-01-8] **$C_7H_4F_3Li$**



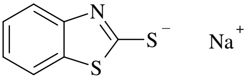
(Preparative hazard for 2-)

See entry ORGANOLITHIUM REAGENTS

See other HALO-ARYLMETALS

2654. Sodium 2-benzothiazolylthiolate

[26249-01-4] **$C_7H_4NNaS_2$**

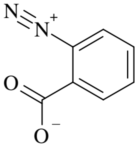


Maleic anhydride

See Maleic anhydride: Bases, etc.

2655. Benzenediazonium-2-carboxylate

[17333-86-7] **$C_7H_4N_2O_2$**



1. Yaroslavsky, S., *Chem. & Ind.*, 1965, 765
2. Sullivan, J. M., *Chem. Eng. News*, 1971, **49**(16), 5
3. Embree, H. D., *Chem. Eng. News*, 1971, **49**(30), 3
4. Mich, T. K. *et al., J. Chem. Educ.*, 1968, **45**, 272
5. Matuszak, C. A., *Chem. Eng. News*, 1971, **49**(24), 39
6. Logullo, F. M. *et al., Org. Synth.*, 1973, Coll. Vol. 5, 54—59

7. Stiles, R. M. *et al.*, 1963, **85**, 1795, footnote 30a
8. Rabideau, P. W., *Org. Prep. Proced. Int.*, 1986, **18**, 113—116

The isolated internal salt is explosive, and should only be handled in small amounts [1]. This has been amply confirmed [2,3]. The salt may be precipitated during the generation of benzyne by diazotisation of anthranilic acid at ambient temperature; some heating is essential for complete decomposition [4]. During decomposition of the isolated salt, too-rapid addition to hot solvent caused a violent explosion [5]. The published procedure [6] must be closely followed for safe working. It was claimed that, contrary to earlier beliefs, diazonium carboxylate hydrohalide salts are also shock-sensitive explosives [7], but this is now firmly refuted. The hydrochloride salt cannot be detonated by impact, but if deliberately ignited by flame contact, it will flash. Thus, when a 30g quantity was ignited, it burned away very rapidly without explosion. The hydrochloride appears to have other practical advantages, in that the yield of dibenzobarrelene, formed from benzyne and naphthalene is much higher when the hydrochloride is used as benzyne precursor, rather than the internal salt [8].

Aniline, or Isocyanides

Huisgen, R. *et al., Chem. Ber.*, 1965, **98**, 4104

It reacts explosively with aniline, and violently with aryl isocyanides.

See other AMINATION INCIDENTS

1-Pyrrolidinylcyclohexene

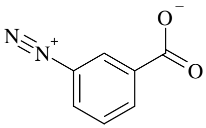
Kuehne, M. E., *J. Amer. Chem. Soc.*, 1962, **84**, 841

Decomposition of benzenediazonium-2-carboxylate in the enamine at 40°C caused a violent explosion.

See other DIAZONIUM CARBOXYLATES

2656. Benzenediazonium-3-carboxylate

[17333-87-8] **$C_7H_4N_2O_2$**



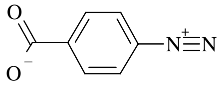
Potassium *O,O*-diphenyl dithiophosphate

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 10)

See other DIAZONIUM CARBOXYLATES

2657. Benzenediazonium-4-carboxylate

[17333-88-9] **$C_7H_4N_2O_2$**



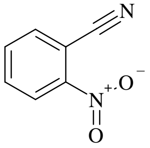
Potassium *O,O*-diphenyl dithiophosphate

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 10)

See other DIAZONIUM CARBOXYLATES

2658. 2-Nitrobenzonitrile

[612-24-8] **$C_7H_4N_2O_2$**



1. Miller, C. S., *Org. Synth.*, 1955, Coll. Vol. 3, 646
2. Partridge, M. W., private comm., 1968

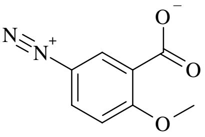
When the published method [1] for preparing the 4- isomer is used to prepare 2-nitrobenzonitrile, a moderate explosion often occurs towards the end of the reaction period. (This may be owing to formation of nitrogen trichloride as a by-product.) Using an alternative procedure, involving heating 2-chloronitrobenzene with copper(I) cyanide in pyridine for 7 h at 160°C, explosions occurred towards the end of the heating period in about 20% of the preparations [2].

See 4-Chloro-3-nitrotoluene: Copper(I) cyanide, Pyridine

See other CYANO COMPOUNDS, NITROARYL COMPOUNDS

2659. 4-Hydroxybenzenediazonium-3-carboxylate

[68596-89-4] **$C_7H_4N_2O_3$**

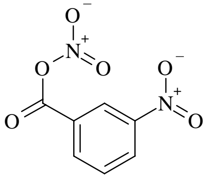


1. Auden, W., *Chem. News*, 1899, **80**, 302
2. Puxeddu, E., *Gazz. Chim. Ital.*, 1929, **59**, 14

It explodes at either 155° [1] or 162°C [2], probably depending on the heating rate.

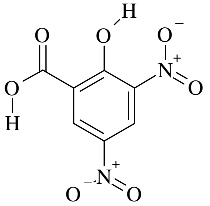
See other DIAZONIUM CARBOXYLATES

2660. 3-Nitrobenzoyl nitrate
[101672-19-9] **$C_7H_4N_2O_6$**



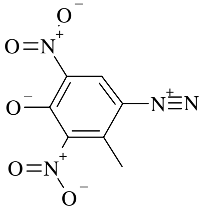
Francis, F. E., *J. Chem. Soc.*, 1906, **89**, 1
The nitrate explodes if heated rapidly, like benzoyl nitrate.
See other ACYL NITRATES, NITROARYL COMPOUNDS

2661. 3,5-Dinitrosalicylic acid (2-Hydroxy-3,5-dinitrobenzoic acid)
[609-99-4] **$C_7H_4N_2O_7$**



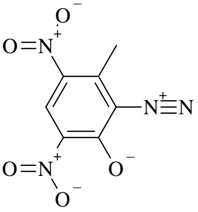
The editor would be surprised if it proved impossible to detonate this analytical reagent, the carboxylation product of 2,4-dinitrophenol, especially in contact with bases. There is no record of problems in use.
See 2,4-Dinitrophenol; 2,4-Dinitrophenylhydrazine
See other POLYNITROARYL COMPOUNDS

2662. 3,5-Dinitro-2-methylbenzenediazonium-4-oxide
[70343-16-7] **$C_7H_4N_4O_5$**



Nielsen, A. T. *et al., J. Org. Chem.*, 1979, **44**, 2503—2504
A very shock-sensitive explosive.
See other ARENEDIAZONIUM OXIDES, POLYNITROARYL COMPOUNDS

2663. 3,5-Dinitro-6-methylbenzenediazonium-2-oxide
[70343-16-7] **$C_7H_4N_4O_5$**

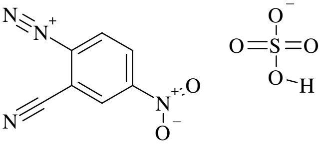


Nielsen, A. T. *et al., J. Org. Chem.*, 1979, **44**, 2503—2504

A very shock-sensitive explosive which melts at 152°C, then decomposes explosively.

See other ARENEDIAZONIUM OXIDES, POLYNITROARYL COMPOUNDS

2664. 2-Cyano-4-nitrobenzenediazonium hydrogen sulfate
[68597-10-4] **$C_7H_4N_4O_6S$**



Sulfuric acid

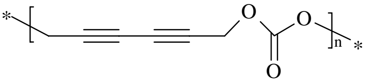
Grewer, T., *Chem. Ing. Tech.*, 1975, **47**, 233—234

DTA examination of a 35% solution of the diazonium salt in sulfuric acid showed 3 exotherms, corresponding to hydrolysis of the nitrile group (peak at 95°), decomposition of the diazonium salt (peak at 160°) and loss of the nitro group (large peak at 240°C). Adiabatic decomposition of the solution from 50°C also showed 3 steps, with induction periods of around 30, 340 and 380 min, respectively.

See THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

See other CYANO COMPOUNDS, DIAZONIUM SULFATES, INDUCTION PERIOD INCIDENTS, NITROARYL COMPOUNDS

2665. Poly(2,4-hexadiyne-1,6-ylene carbonate) (Poly(oxycarbonyl-2,4-hexadiyne-1,6-diyl))
[63354-77-8] **$(C_7H_4O_3)_n$**

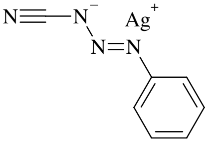


Kuehling, S. *et al., Macromolecules*, 1993, **23**(19), 4192

This polymer, prepared by copper catalysed air oxidation of dipropynyl carbonate, exploded readily on warming or manipulation. The corresponding adipate and

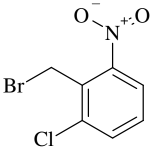
sebacate esters are non-explosive. The authors wonder if peroxide formation is involved; such explanation seems otiose.
See other ACETYLENIC COMPOUNDS

2666. Silver 3-cyano-1-phenyltriazen-3-ide
[70324-20-8] **$C_7H_5AgN_4$**



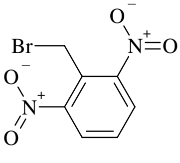
Bretschneider, H., *Monats.*, 1950, **81**, 981
It is explosive.
See other CYANO COMPOUNDS, SILVER COMPOUNDS, TRIAZENES

2667. 6-Chloro-2-nitrobenzyl bromide
[56433-01-3] **$C_7H_5BrClNO_2$**



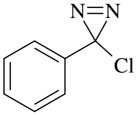
See entry NITROBENZYL COMPOUNDS (reference 2)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2668. 2,6-Dinitrobenzyl bromide
[3013-38-5] **$C_7H_5BrN_2O_4$**



Potassium phthalimide
Reich, S. *et al., Bull. Soc. Chim. Fr. [4]*, 1917, **21**, 119
Reaction temperature in absence of solvent must be below 130—135°C to avoid explosive decomposition.
See entry NITROBENZYL COMPOUNDS
See other POLYNITROARYL COMPOUNDS

2669. Phenylchlorodiazirine
[4460-46-2] **$C_7H_5ClN_2$**



1. Wheeler, J. J., *Chem. Eng. News*, 1970, **48**(30), 10
2. Manzara, A. P., *Chem. Eng. News*, 1974, **52**(42), 5
3. Padwa, A. *et al., Org. Synth.*, 1981, **60**, 53—57

The neat material is about three times as shock-sensitive as glyceryl nitrate, and should not be handled undiluted [1]. It exploded during vacuum distillation at 3.3 mbar from a bath at 140°C. Impact- and spark-sensitivities were determined, and autoignition occurred after 30 s at 107°C [2]. An explosion occurred during distillation at a pot temperature of 80°C. Full handling precautions are detailed. Dilution of neat material with solvent eliminates shock-sensitivity [3].

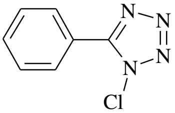
See other AUTOIGNITION INCIDENTS

Phenylacetylene

See 3-Chloro-1,3-diphenylcyclopropene

See other DIAZIRINES

2670. *N*-Chloro-5-phenyltetrazole
[65037-43-6] **$C_7H_5ClN_4$**

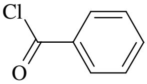


Gallacher, T. C. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 420

Thermal decomposition is vigorous, and was explosive on one occasion.

See other N-HALOGEN COMPOUNDS, TETRAZOLES

2671. Benzoyl chloride
[98-88-4] **C_7H_5ClO**



Aluminium chloride, Naphthalene

See Aluminium chloride: Benzoyl chloride, etc.

Dimethyl sulfoxide MRH 1.30/tr.

See Dimethyl sulfoxide: Acyl halides

Other reactants

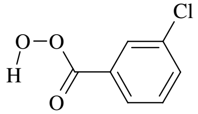
Yoshida, 1980, 58

MRH values calculated for 13 combinations with oxidants are given.

See other ACYL HALIDES

2672. 3-Chloroperoxybenzoic acid

[937-14-4] **$C_7H_5ClO_3$**



Kubota, A *et al., Org. Proc. Res. & Dev.*, 2004, **8**(6), 1076

During oxidation of a sulfide to a sulfoxide, it was found that the peracid, in DMF, was dangerously unstable. It was shown it could convert to the dibenzoylperoxide, probably of lesser reactivity, thus permitting a build-up of potential energy during a semi-batch process. However, the explosion seems to have occurred in the reagent solution, not yet added to the sulfide. Peroxide formation might provide an explanation for the earlier incident reported below, but seems less satisfactory here. Like other formates, DMF is a reducant. Replacement of DMF by dichloromethane permitted scale-up.

2-Bromo-4-methylpyridine

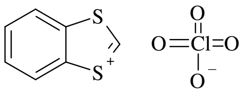
1. Brand, W. W., *Chem. Eng. News*, 1978, **56**(24), 88
2. Shanley, E. S., *Chem. Eng. News*, 1978, **56**(29), 43

Vacuum evaporation of the product of unheated conversion of the pyridine to its *N*-oxide with 5% excess of the peroxy acid in chloroform gave a residue which decomposed violently [1]. This was attributed to the relative stability of the peroxy acid in the cold pure state, which when concentrated and finally heated with other materials underwent accelerating decomposition [2].

See other PEROXYACIDS

2673. 1,3-Benzodithiolium perchlorate

[32283-21-9] **$C_7H_5ClO_4S_2$**

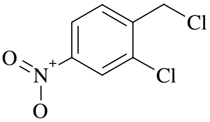


1. Pelter, A., *Chem. Abs.*, 1981, **95**, 97643 (ref. there to *Tetrahedron Lett.* original is incorrect)
2. Degari, I. *et al., J. Chem. Soc., Perkin Trans. 1*, 1976, 1886
3. Anon., *Univ. Safety Assoc. Safety News*, 1978, (10), 11—12

Highly friction sensitive, with considerable explosion hazard [1]. Repeating a published method ([2], where explosion at the m.p., 180°C is noted), the product was dried in a desiccator. When the lid (ground glass flange) was slid off, the friction initiated explosion of a little of the compound deposited on the flange, and a severe explosion resulted [3].

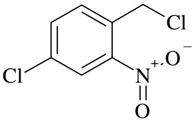
See other GLASS INCIDENTS, NON-METAL PERCHLORATES

2674. 2-Chloro-4-nitrobenzyl chloride
[50274-95-8] **$C_7H_5Cl_2NO_2$**



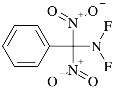
See entry NITROBENZYL COMPOUNDS (reference 2)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2675. 4-Chloro-2-nitrobenzyl chloride
[938-71-6] **$C_7H_5Cl_2NO_2$**



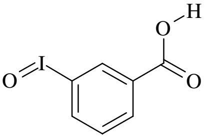
See entry NITROBENZYL COMPOUNDS (reference 2)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2676a. α-(Difluoroamino)-α,α-dinitrotoluene
((Difluoroaminodinitromethyl)benzene)
(*N,N*-Difluoro-α,α-dinitrobenzenemethanamine)
[157066-32-5] **$C_7H_5F_2N_3O_4$**



See 1,1-DINITRODIFLUORAMINES
See other *N*-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

2676b. Iodoxybenzoic acid (Iodosobenzoic acid)
[64297-65-0] **$C_7H_5IO_3$**

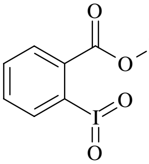


Cain, G. A. *et al., Chem. Eng. News*, 2002, **80**(26), 4

A sample prepared on a 200 g scale and dried on the filter exploded while being transferred with a spoon. It was previously known to deflagrate at its melting point (225°C), like other iodosobenzenes.

See other IODINE COMPOUNDS

2677. 2-Iodylbenzoic acid (1-Hydroxy-1,2-benziodoxol-3-one-1-oxide) [64297-64-9] (Acid) [131-62-4] (Iodoxolone) $C_7H_5IO_4$



Plumb, J. B., *Chem. Eng. News*, 1990, **68**(29), 3

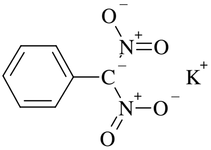
The pure dry acid explodes at 233°C, and violently if confined, possibly $< 200°C$. It is also impact-sensitive, exploding under a hammer blow, or under impact of a 534 g steel ball falling from a height of 1 m. Several of its salts (ammonium, potassium, sodium, silver, barium, calcium and magnesium) are also explosive. The acid is precursor to the 'Dess-Martin periodinane' mild oxidant, and is produced when the latter is treated with water.

Calcium 2-iodylbenzoate

See 1,1,1-Triacetoxy-1,2-benziodoxol-3-one

See other IODINE COMPOUNDS, ORGANIC ACIDS

2678. Potassium phenyldinitromethanide [28198-51-8] $C_7H_5KN_2O_4$

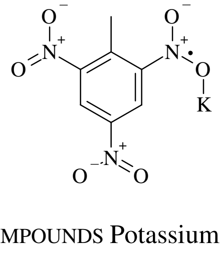


Rohman, A. *et al., J. Org. Chem.*, 1976, **41**, 124

It is unwise to use more than 0.02 mol of potassium salts of dinitroalkanes as they are explosive.

See related aci-NITRO SALTS, POLYNITROALKYL COMPOUNDS

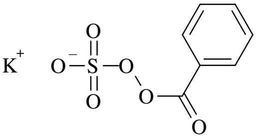
2679. Potassium 2,4,6-trinitrotoluene [ ] $C_7H_5KN_3O_6$



See entry POLYNITROARYL COMPOUNDS Potassium radical salts

2680. Potassium *O—O*-benzoylmonoperoxosulfate

[ ] **$C_7H_5KO_5S$**



Alone, or Sulfuric acid

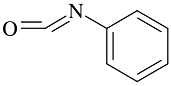
Willstätter, R. *et al., Ber.*, 1909, **42**, 1839

The anhydrous salt explodes on grinding, and the monohydrate on heating to 70—80°C, or in contact with sulfuric acid.

See other DIACYL PEROXIDES, PEROXOACID SALTS

2681. Phenyl isocyanate

[103-71-9] **C_7H_5NO**



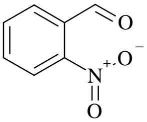
Energy of decomposition (in range 240—460°C) measured as 0.41 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other ORGANIC ISOCYANATES

2682. 2-Nitrobenzaldehyde

[552-89-6] **$C_7H_5NO_3$**



1. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
2. Grewer. T. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 657—664, Basle, SSCI, 1980
3. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987
4. Anon., *Loss Prev. Bull.*, 1989, (087), 27—29

Energy of decomposition (in range 220—370°C) measured as 2.124 kJ/g by DSC, and T_{ait24} was determined as 123°C by adiabatic Dewar tests, with an apparent energy of activation of 116 kJ/mol [1]. Initial decomposition temperature by ARC was 176°C. A very high rate of pressure increase was observed in exothermic decomposition, and further work on homogeneous decomposition under confinement has been reported [2,3]. Exothermic decomposition during vacuum distillation of an atypical 600 kg

batch of 2-nitrobenzaldehyde containing other isomers, and which accelerated to explosion, has been reported and discussed [4].
See entry NITROBENZALDEHYDES

Active carbon

Mixtures with active carbon (1.5:1 mol) deflagrate at 1.25 cm/min.
See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 3)

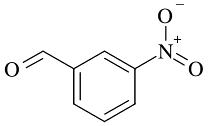
Pyrrole

Sorrell, T. N., *Inorg. Synth.*, 1980, **20**, 162

In the preparation of 5,10,15,20-tetrakis(2-nitrophenyl)porphyrin by dropwise addition of the aldehyde in acetic acid, the exothermic reaction may become so violent that solvent sprays out of the condenser. However, a low yield may ensue if the reaction is insufficiently vigorous, so a careful compromise is required.
See other ALDEHYDES, NITROARYL COMPOUNDS

2683. 3-Nitrobenzaldehyde

[99-61-6] **$C_7H_5NO_3$**

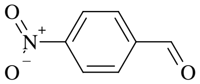


1. Lange, J. *et al., Chem. & Ind.*, 1967, 1424
2. Klais, O. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C24—C34, Rugby, IChE, 1983
3. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

Delays in working up the crude product caused violent explosions during attempted vacuum distillation. An alternative method of crystallisation is described [1]. There is a very high rate of pressure increase in exothermic decomposition [2]. Energy of decomposition (in range 180—420°C) measured as 2.19 kJ/g by DSC, and T_{ait24} was determined as 147°C by adiabatic Dewar tests, with an apparent energy of activation of 168 kJ/mol [3]. The initial decomposition temperature by ARC was 166°C.
See entry NITROBENZALDEHYDES
See other ALDEHYDES, NITROARYL COMPOUNDS

2684. 4-Nitrobenzaldehyde

[555-16-8] **$C_7H_5NO_3$**



Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

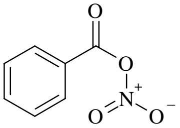
Energy of decomposition (in range 220—450°C) measured as 1.602 kJ/g by DSC, and T_{ait24} was determined as 171°C by adiabatic Dewar tests, with an apparent energy of activation of 202 kJ/mol [1]. The initial decomposition temperature by ARC was 226°C. A very high rate of pressure increase was observed in exothermic decomposition.

See entries NITROBENZALDEHYDES, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

See other ALDEHYDES, NITROARYL COMPOUNDS

2685. Benzoyl nitrate

[6786-32-9] **$C_7H_5NO_4$**



1. Francis, F. E., *J. Chem. Soc.*, 1906, **89**, 1
2. Ferrario, E., *Gazz. Chim. Ital. [1]*, 1901, **40**, 99

An unstable liquid which is capable of distillation under reduced pressure, but which explodes violently on rapid heating at ambient pressure [1]. It may also explode on exposure to light [2].

See other IRRADIATION DECOMPOSITION INCIDENTS

Water

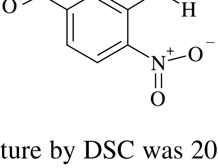
Francis, F. E., *J. Chem. Soc.*, 1906, **89**, 1

Reactivity of benzoyl nitrate towards moisture is so great that attempted filtration through an undried filter paper causes explosive decomposition (possibly involving cellulose nitrate?).

See other ACYL NITRATES

2686. 3-Hydroxy-4-nitrobenzaldehyde

[704-13-2] **$C_7H_5NO_4$**



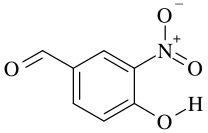
Initial decomposition temperature by DSC was 200°C.

See entry NITROBENZALDEHYDES

See other ALDEHYDES, NITROARYL COMPOUNDS

2687. 4-Hydroxy-3-nitrobenzaldehyde

[3011-34-5] **$C_7H_5NO_4$**

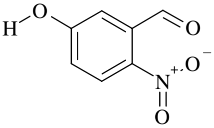


Initial decomposition temperature by DSC was 200°C.

See entry NITROBENZALDEHYDES *See other* ALDEHYDES, NITROARYL COMPOUNDS

2688. 5-Hydroxy-2-nitrobenzaldehyde

[42454-06-8] **$C_7H_5NO_4$**

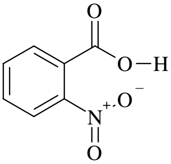


Initial decomposition temperature by DSC was 175°C.

See entry NITROBENZALDEHYDES *See other* NITROARYL COMPOUNDS

2689. 2-Nitrobenzoic acid

[552-16-9] **$C_7H_5NO_4$**



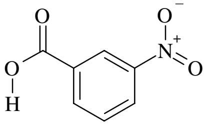
Energy of decomposition (in range 230—450°C) measured as 1.72 kJ/g by DSC, and T_{ait24} was determined as 189°C by adiabatic Dewar tests, with an apparent energy of activation of 156 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other NITROARYL COMPOUNDS, ORGANIC ACIDS

2690. 3-Nitrobenzoic acid

[121-92-6] **$C_7H_5NO_4$**



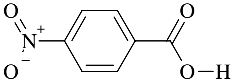
Energy of decomposition (in range 320—410°C) measured as 1.734 kJ/g by DSC, and T_{ait24} was determined as 245°C by adiabatic Dewar tests, with an apparent energy of activation of 151 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other NITROARYL COMPOUNDS, ORGANIC ACIDS

2691. 4-Nitrobenzoic acid

[62-23-7] **$C_7H_5NO_4$**



Energy of decomposition (in range 320—360°C) measured as 2.234 kJ/g by DSC, and T_{ait24} was determined as 247°C by adiabatic Dewar tests, with an apparent energy of activation of 131 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Potassium hydroxide

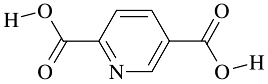
Mixtures of the acid with potassium hydroxide (1:2 mol) readily deflagrated, at a rate of 5.1 cm/min.

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 3)

See other DEFLAGRATION INCIDENTS, NITROARYL COMPOUNDS, ORGANIC ACIDS

2692. 2,5-Pyridinedicarboxylic acid

[100-26-5] **$C_7H_5NO_4$**



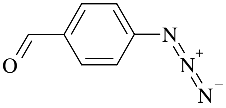
Preparative hazard

See Nitric acid: 5-Ethyl-2-methylpyridine

See other ORGANIC ACIDS

2693. 4-Azidobenzaldehyde

[24173-36-2] **$C_7H_5N_3O$**



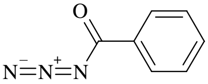
Lahti, P. M., *Chem. Eng. News*, 1998, **76**(28), 8

Very shock sensitive; explodes in drop-weight test at 11 kg-cm.

Energy of decomposition (in range 110—220°C) measured as 1.67 kJ/g.

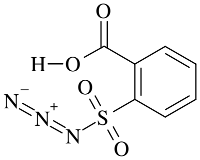
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ALDEHYDES, ORGANIC AZIDES

2694. Benzoyl azide
[582-61-6] **$C_7H_5N_3O$**



Bergel, F., *Angew. Chem.*, 1927, **40**, 974
The sensitivity towards heat of this explosive compound is increased by previous compression, confinement and presence of impurities. Crude material exploded violently between 120 and 165°C.
See other ACYL AZIDES, CATALYTIC IMPURITY INCIDENTS

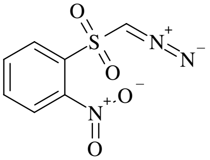
2695. Carboxybenzenesulfonyl azide (Azidosulfonylbenzoic acid)
[56743-33-0] [17202-49-2] 4-isomer **$C_7H_5N_3O_4S$**



Anon., *Res. Discl.*, 1975, **134**, 44
The azide (structure not stated) is not impact-sensitive, but decomposes explosively at 120°C. Blending with 75% of polymer as diluent eliminated the explosive decomposition.
See other ACYL AZIDES

Preparative hazard
Tuma, L. D. *et al., Synlett*, 1996, (5), 407
During preparations of the 4-carboxy isomer, it was found that some of the exceptionally dangerous 4-azidobenzenesulfonylazide appeared as a byproduct, due to presence of 4-chlorinated impurity in the starting material.

2696. 2-Nitrophenylsulfonyldiazomethane
[49558-46-5] **$C_7H_5N_3O_4S$**



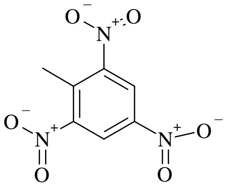
Wagenaar, A. *et al., J. Org. Chem.*, 1974, **39**, 411—413

Severe explosions occurred when the cold crystalline solid was allowed to warm to ambient temperature. Normal manipulation of dilute solutions appears feasible, but the solid must be handled at lowest possible temperatures with full safety precautions. The 4- isomer appears much more stable.

See other DIAZO COMPOUNDS, NITROARYL COMPOUNDS

2697. 2,4,6-Trinitrotoluene

[118-96-7] **$C_7H_5N_3O_6$**



NSC 314, 1981

Heat of decomposition was determined as 5.1 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 1)

Added impurities

Haüptli, H., private comm., 1972

During investigation of effect of 1% of added impurities on the thermal explosion temperature of TNT (297°C), it was found that fresh red lead, sodium carbonate and potassium hydroxide reduced the explosion temperatures to 192, 218, and 192°C, respectively.

See Potassium: Nitrogen-containing explosives

See other CATALYTIC IMPURITY INCIDENTS

Bases MRH Sodium hydroxide 5.40/tr.

Capellos, C. *et al., Chem. Abs.*, 1982, **96**, 88003

The formation of *aci*-quinonoid transient intermediates by electronic excitation has been identified spectroscopically. Proton abstractors (bases) such as sodium hydroxide, potassium iodide or tetramethylammonium octahydrotriborate induce deflagration in molten TNT.

See NITROAROMATIC—ALKALI HAZARDS

Metals, Nitric acid

Kovache, A. *et al., Mém.* Poudres, 1952, **34**, 369—378

Trinitrotoluene in contact with nitric acid and lead or iron produces explosive substances which may readily be ignited by shock, friction or contact with nitric or sulfuric acids. Such materials have been involved in industrial explosions.

See HEAVY METAL DERIVATIVES

Other reactants

Yoshida, 1980, 254

MRH values calculated for 3 combinations with catalytically active materials are given.

Potassium hydroxide

Copisarow, M., *Chem. News*, 1915, **112**, 283—284

TNT and potassium hydroxide in methanol will interact even at —65°C to give explosive *aci*-nitro salts (presumably *o*-quinonoid, or possibly Meisenheimer complexes). The explosion temperature is lowered to 160°C by the presence of a little potassium hydroxide.

See entry aci-NITROQUINONOID COMPOUNDS

Sodium carbonate, Water

Iida, M. *et al., Chem. Abs.*, 1997, **127**, 222627q

TNT reacts vigorously with sodium carbonate, in presence of water at 100°C and above. The solid residue resulting ignites on contact with strong acid.

See 2,4,5-Trinitrotoluene; next below

See NITROAROMATIC—ALKALI HAZARDS

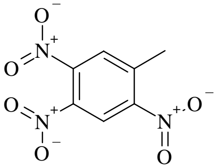
Sodium dichromate, Sulfuric acid

See Sodium dichromate: Sulfuric acid, Trinitrotoluene

See other POLYNITROARYL COMPOUNDS

2698. 2,4,5-Trinitrotoluene

[610-25-3] **$C_7H_5N_3O_6$**



Sodium carbonate

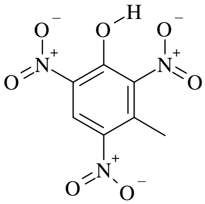
Biasutti, 1981, 78

Sodium carbonate was added to a heated tank of washed TNT to neutralise excess acidity. It is known that the assym. isomer of TNT reacts with sodium carbonate to form unstable compounds, and decomposition led to a fire and detonation of 5 tonnes of explosive.

See other NITROAROMATIC—ALKALI HAZARDS, POLYNITROARYL COMPOUNDS

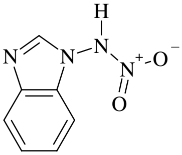
2699. 3-Methyl-2,4,6-trinitrophenol

[602-99-3] **$C_7H_5N_3O_7$**



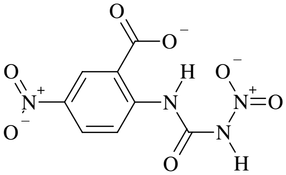
Sorbe, 1968, 153
It explodes above 150°C.
See other POLYNITROARYL COMPOUNDS

2700. Benzimidazolium 1-nitroimidate
[52096-22-7] **$C_7H_5N_4O_2$**



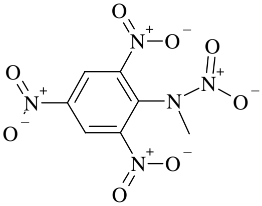
It explodes at the m.p., 169°C.
See entry N-AZOLIUM NITROIMIDATES

2701. 1-Nitro-3-(2,4-dinitrophenyl)urea
[22751-18-4] **$C_7H_5N_5O_7$**



McVeigh, J. L *et al., J. Chem. Soc.*, 1945, 621
It is an explosive of lower power, but of greater impact- or friction-sensitivity than picric acid, so should not be stored in bottles with ground-in stoppers.
See other N—NITRO COMPOUNDS, POLYNITROARYL COMPOUNDS

2702. *N*,2,4,6-Tetranitro-*N*-methylaniline (Tetryl)
[479-45-8] **$C_7H_5N_5O_8$**

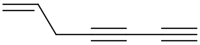


Hydrazine
See Hydrazine: Oxidants

Trioxygen difluoride
See ‘Trioxygen difluoride’: Various materials
See other N-NITRO COMPOUNDS, POLYNITROARYL COMPOUNDS

2703. 1-Heptene-4,6-diyne

[ ] **C_7H_6**



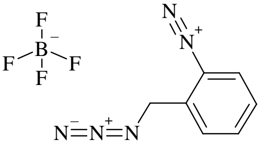
1. Armitage, J. B. *et al., J. Chem. Soc.*, 1952, 1994
2. *CHETAH*, 1990, 182

It decomposes explosively with great ease [1] but was shown to be exploded by a detonator, not by mechanical shock [2].

See other ALKYNES, ALLYL COMPOUNDS

2704. 2-Azidomethylbenzenediazonium tetrafluoroborate

[59327-98-9] **$C_7H_6BF_4N_5$**



Trichloroacetonitrile

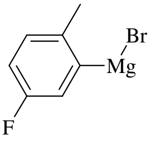
Kreher, R. *et al., Tetrahedron Lett.*, 1976, 4260

Thermal decomposition of the salt in nitriles produces 2-substituted quinazolines. In trichloroacetonitrile it proceeded explosively.

See other DIAZONIUM TETRAHALOBORATES, ORGANIC AZIDES

2705. 5-Fluoro-2-methylphenylmagnesium bromide (Bromo(5-fluoro-2-methylphenyl) magnesium)

[ ] **C_7H_6BrFMg**



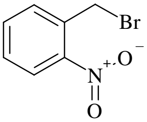
Preparative Hazard

Jasiewicz, M. L. *Chem. & Ind.*, 1995, 246

A considerable explosion resulted from preparation of this compound (which presumably exists with several tightly complexed solvent molecules) in limited tetrahydrofuran under reflux. Investigation showed that there is an exotherm at 130°C, giving 440 J/g, followed by a more violent one at 300°C giving 690 J/g. Using a large excess of solvent no problems are observed.

See other GRIGNARD REAGENTS

2706. 2-Nitrobenzyl bromide
[3958-60-9] **$C_7H_6BrNO_2$**



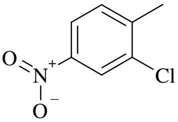
1. Biasutti, 1981, 114
2. Cardillo, P. *et al., Rivista Combust.*, 1982, **36**, 304
3. Cardillo. P. *et al., Proced. 34th Ital. Chem. Congr., 'Safety of Chemical Processes'*, 71—82, Milan, 1983

During the first large scale preparation of the bromide from 2-nitrotoluene, the reactor exploded violently, though hundreds of runs had been done uneventfully in a pilot scale plant [1]. Following a thermal explosion during drying of the compound at a slightly elevated temperature, its thermal stability has been determined by TGA, DSC and ARC techniques. The latter shows that exothermic decomposition begins at 100°C and proceeds in two stages with abundant gas evolution. The former techniques indicate onset of decomposition at 130° and 112°C, respectively [2]. Further work on the 3- and 4- isomers showed them to be marginally more stable than the 2- nitro compound.

See 2-Nitrobenzyl chloride

See other GAS EVOLUTION INCIDENTS, NITROARYL COMPOUNDS, NITROBENZYL COMPOUNDS

2708a. 2-Chloro-4-nitrotoluene
[121-86-8] **$C_7H_6ClNO_2$**



Other reactants

Yoshida, 1980, 112

MRH values calculated for 13 combinations with oxidants are given.

Sodium hydroxide MRH 3.39/tr.

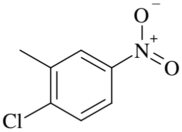
1. Anon., *ABCM Quart. Safety Summ.*, 1962, **33**, 20
2. *MCA Case History No. 907*

The residue from vacuum distillation of crude material (contaminated with sodium hydroxide) exploded after showing signs of decomposition. Experiment showed that 2-chloro-4-nitrotoluene decomposes violently when heated at 170—200°C in presence of alkali. Thorough water washing is therefore essential before distillation is attempted [1]. A similar incident was reported with mixed chloronitrotoluene isomers [2].

See other NITROAROMATIC—ALKALI HAZARDS, NITROARYL COMPOUNDS

2708b. 2-Chloro-5-nitrotoluene

[13290-74-9] **$C_7H_6ClNO_2$**



Dimethyl sulfoxide, Potassium hydroxide

1. Anon., Chem Brit, 1999, 35(8), 8
2. Editor's comments.

It is reported that an industrial explosion was initiated by charging potassium hydroxide in place of potassium carbonate to the chloro-nitro compound in the sulfoxide [1]. Dry potassium carbonate is a useful base for nucleophilic displacement of chlorine in such systems, reaction being controlled by addition of the nucleophile. The carbonate is not soluble in DMSO and possesses no significant nucleophilic activity itself. Hydroxides have, to create phenoxide salts as the first product. These are better nucleophiles than their progenitor, and also base-destabilised nitro compounds. Result: heat and probable loss of control. As it nears its boiling point DMSO also becomes susceptible to exothermic breakdown, initially to methanethiol and formaldehyde. Methanethiolate is an even better nucleophile than a phenoxide and also a fairly proficient reducer of nitro-groups, while formaldehyde condenses with phenols under base catalysis in a reaction which has itself caused many an industrial runaway and explosion. There is thus a choice of routes to disaster. Industrial scale nucleophilic substitution on chloro-nitroaromatics has previously demonstrated considerable hazard in presence of water or hydroxide, even in solvents not themselves prone to exothermic decomposition [2].

2,4,-Dichloronitrobenzene

Formaldehyde

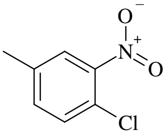
Phenol

See Dimethyl sulfoxide

See other aci-NITROQUINONOID COMPOUNDS, HALOARYL COMPOUNDS, NITROARYL COMPOUNDS, RUNAWAY REACTIONS

2709. 4-Chloro-3-nitrotoluene

[89-60-1] **$C_7H_6ClNO_2$**



Copper(I) cyanide, Pyridine

1. Hub, L., *Proc. Chem. Process. Haz. Symp. VI* (Manchester, 1977), No. 49, 39—46, Rugby, IChE, 1977
2. Hub, L., private comm., 1977

Industrial preparation of 4-cyano-3-nitrotoluene by heating the reaction components at around 170°C for 6 h led to an explosion in 1976. Subsequent investigation by DSC showed that the cyano compound in presence of the starting materials exhibited an exotherm at 180°C. After 6 h reaction, this threshold temperature fell to 170°C. Isothermal use of a safety calorimeter showed that a large exotherm occurred during the first hour of reaction and that, in absence of strong cooling, the reaction accelerated and the vessel contents were ejected by the vigour of the decomposition [2].

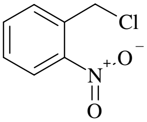
See 2-Nitrobenzonitrile,

See REACTION SAFETY CALORIMETRY

See other NITROARYL COMPOUNDS

2710a. 2-Nitrobenzyl chloride

[612-23-7] **$C_7H_6ClNO_2$**



Cardillo, P. *et al., Proc. 34th Ital. Chem. Congr., 'Safety of Chem. Processes'*, 71—82, Milan, 1983

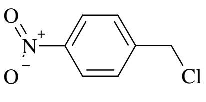
Following an explosion during drying of 2-nitrobenzyl bromide, the thermal stability of all six isomeric nitrobenzyl halides was investigated by TGA, DSC and ARC techniques. All the halides decomposed exothermally with abundant gas evolution, and the 2-nitro chloride is less thermally stable than the 3- or 4- isomers.

See 2-Nitrobenzyl bromide

See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS, NITROBENZYL COMPOUNDS

2710b. 4-Nitrobenzyl chloride

[100-14-1] **$C_7H_6ClNO_2$**

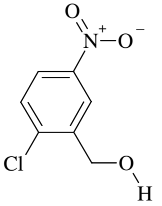


T_{ait24} was determined as 189°C by adiabatic Dewar tests, with an apparent energy of activation of 124 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

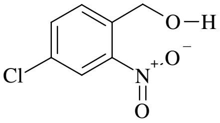
See other NITROARYL COMPOUNDS, NITROBENZYL COMPOUNDS

2711. 2-Chloro-5-nitrobenzyl alcohol
[80866-80-4] **$C_7H_6ClNO_3$**



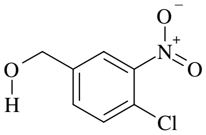
See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2712. 4-Chloro-2-nitrobenzyl alcohol
[22996-18-5] **$C_7H_6ClNO_3$**



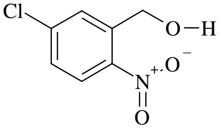
See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2713. 4-Chloro-3-nitrobenzyl alcohol
[55912-20-4] **$C_7H_6ClNO_3$**



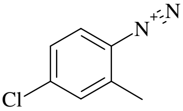
See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2714. 5-Chloro-2-nitrobenzyl alcohol
[73033-58-6] **$C_7H_6ClNO_3$**



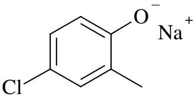
See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2715. 4-Chloro-2-methylbenzenediazonium salts
[27165-08-8] (ion) **$C_7H_6ClN_2^+ Z^-$**



Sodium hydrogen sulfide, or Sodium disulfide, or Sodium polysulfide
See entry DIAZONIUM SULFIDES AND DERIVATIVES (references 1—4)
See other DIAZONIUM SALTS

2716a. Sodium 4-chloro-2-methylphenoxide
[52106-86-2] **C_7H_6ClNaO**

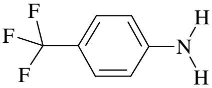


Anon., private comm., 1984

A dry solution of the sodium salt in n-butanol was usually prepared by azeotropic drying. Use of excessively wet recovered butanol led to complete removal of the butanol with the water and heating of the dry salt at 200°C, when rapid decomposition occurred, leaving a glowing carbonised residue.

See 4-Chloro-2-methylphenol: Sodium hydroxide

2716b. 4-Trifluoromethylaniline (4-Trifluoromethylbenzeneamine)
[455-14-1] **$C_7H_6F_3N$**

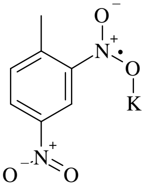


Tickner, D. et al., Org. Process R. & D., 2001, 5(3), 270

A part used polythene drum of this, usually received as an oil, was discovered to be crystalline after six months storage. The drum was warmed in an air drier at 55°C for sixteen hours. This did not melt it (the melting point is debated, but lower than this). About five hours later, having spent this time in ambient temperatures, the bottom of the drum blew out with vigorous emission of white fumes. DSC on authentic trifluoromethylaniline showed an exotherm around 180°C, the temperature declining on ageing. The solid from the drum gave a somewhat smaller one at 90°C. The solid is thought to be a trimer in which one trifluoromethyl group has condensed with two amines to form an imidine structure, and hydrogen fluoride. Solidification of the aniline should be regarded as a warning sign.

2717. Potassium 2,6-dinitrotoluene

[ ] **$C_7H_6KN_4O_4$**

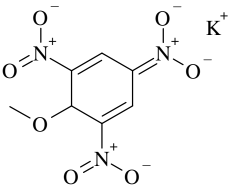


The o- and m- isomers are similar.

See entry POLYNITROARYL COMPOUND Potassium radical salts

2718. Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide

[1270-21-9] **$C_7H_6KN_3O_7$**



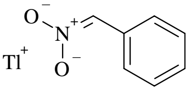
1. Meisenheimer, J., *Ann.*, 1902, **323**, 221
2. Millor, H. D. *et al., Sidgwick's Organic Chemistry of Nitrogen*, 396, Oxford, Clarendon Press, 3rd edn, 1966

The product of interaction of trinitrobenzene and conc. aqueous potassium hydroxide in methanol is explosive, and analyses as the hemihydrate of a hemiacetal of the *aci-p*-quinonoid form of picric acid [1], and/or the mesomeric *o*-forms [2].

See other aci-NITROQUINONOID COMPOUNDS, POLYNITROARYL COMPOUNDS

2719. Thallium *aci*-phenylnitromethanide

[53847-48-6] **$C_7H_6NO_2Tl$**

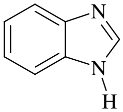


McKillop, A. *et al., Tetrahedron*, 1974, **30**, 1369

No attempt should be made to isolate or dry this compound, as it is treacherously explosive.

See other aci-NITRO SALTS, HEAVY METAL DERIVATIVES

2720. Benzimidazole (Benzodiazole)
[51-17-2] **$C_7H_6N_2$**



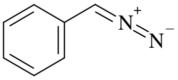
CHETAH, 1990, 188

Shock sensitive (which seems unlikely but not impossible; it is modestly endothermic: ΔH_f° 80 kJ/mole, 0.7 kJ/g).

See Benzotriazole

See other ENDOTHERMIC COMPOUNDS

2721. Phenyldiazomethane
[766-91-6] **$C_7H_6N_2$**

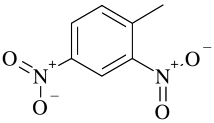


Schneider, M. *et al., Tetrahedron*, 1976, **36**, 621

The need for care in distillation of phenyldiazomethane is stressed. Previously it has been used as prepared in solution.

See other DIAZO COMPOUNDS

2722. 2,4-Dinitrotoluene
[121-14-2] **$C_7H_6N_2O_4$**



(*MCA SD-93*, 1966); *NSC 658*, 1976

1. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
2. *MCA SD-93*, 1966
3. Biasutti, 1981, 143
4. Bond, J., *Loss Prev. Bull.*, 1983, 050, 18
5. Anon., *Loss Prevention Bull.*, 1989, **88**, 13

T_{ait24} was determined as 181°C by adiabatic Dewar tests, with an apparent energy of activation of 153 kJ/mol [1]. The commercial material, containing some 20% of the 2,6- isomer, decomposes at 250°, but at 280°C decomposition becomes self-sustaining. Prolonged heating below these temperatures may also cause some decomposition, and the presence of impurities may decrease the decomposition temperatures [2]. Although not considered to be explosive, several cases of detonation in manufacture or storage have been reported [3], including an explosion when a jug of dinitrotoluene was dropped into a machine [4]. An isolated pipe filled with crude dinitrotoluene at a temperature between 125 and 135°C ran away to detonation over 3.5 hours. Having been separated from spent acid, but not washed, it contained traces of both sulfuric and nitric acids. Investigation showed that this combination destabilised the material more than either separately. A sample (2 phase) of approximate composition dinitrotoluene 45%, nitric acid 5%, sulfuric acid 40%, water 10% showed an exothermic reaction on ARC as low as 66°C [5].

Alkali

Bateman, T. L. *et al., Loss. Prev.*, 1974, **8**, 117—122

Dinitrotoluene held at 210°C (rather than the 125° intended) for 10 days in a 50 mm steam-heated transfer pipeline exploded. Subsequent tests showed decomposition at 210°C (producing a significant pressure rise) in 1 day, and presence of sodium carbonate (but not rust) reduced the induction period. A maximum handling temperature of 150°C was recommended, (when the induction period was 32 days, or 14 days for alkali-contaminated material).

See other CATALYTIC IMPURITY INCIDENTS, INDUCTION PERIOD INCIDENTS, NITROAROMATIC—ALKALI HAZARDS

Nitric acid MRH 4.56/tr.

See Nitric acid: Nitroaromatics

Other reactants

Yoshida, 1980, 159

MRH values calculated for 10 combinations, largely with catalytically active materials, are given.

Sodium oxide

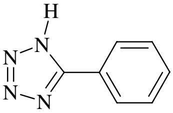
Anon., *Rept. of Explos. Div.*, Ottawa, Dept. of Mines, 1929

Admixture of the two solids caused a rapid reaction and fire.

See other NITROAROMATIC—ALKALI HAZARDS, POLYNITROARYL COMPOUNDS

2723. 5-Phenyltetrazole

[3999-10-8] **$C_7H_6N_4$**



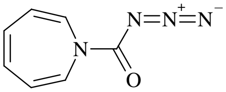
Wedekind. E., *Ber.*, 1898, **31**, 948

It explodes on attempted distillation.

See other TETRAZOLES

2724. *N*-Azidocarbonylazepine

[ ] **$C_7H_6N_4O$**



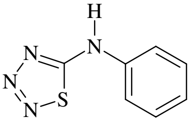
Chapman, L. E. *et al., Chem. & Ind.*, 1966, 1266

It explodes on attempted distillation.

See other ACYL AZIDES

2725. *N*-Phenyl-1,2,3,4-thiatriazolamine (Phenylaminothia-2,3,4-triazole)

[13078-30-3] **$C_7H_6N_4S$**



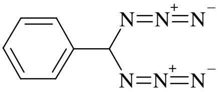
CHETAH, 1990, 182

Shock sensitive.

See other HIGH NITROGEN COMPOUNDS, N—S COMPOUNDS

2726. Phenyldiazidomethane

[17122-97-3] **$C_7H_6N_6$**



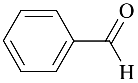
Barash, L. *et al., J. Amer. Chem. Soc.*, 1967, **89**, 3391

A sample of the *gem*-diazide detonated on contact with a hot glass surface during ampoule sealing operations.

See other ORGANIC AZIDES

†2727. Benzaldehyde

[100-52-7] **C_7H_6O**



HCS 1980, 191

Other reactants

Yoshida, 1980, 333

MRH values calculated for 14 combinations with oxidants are given.

Peroxyformic acid MRH 5.69/99+

See Peroxyformic acid: Organic materials

Propionic acid, Pyrrolidine

Kaufman, J. A., private comm., 1987

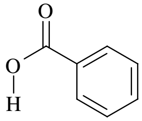
An explosion occurred when benzaldehyde, pyrrolidine (pyrrole ?) and propionic acid were heated to form porphins.

See 2-Nitrobenzaldehyde: Pyrrole

See other ALDEHYDES, REDUCANTS

2728. Benzoic acid

[65-85-0] **$C_7H_6O_2$**



HCS 1980, 191

The finely powdered dry acid is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

Other reactants

Yoshida, 1980, 32

MRH values calculated for 12 combinations with oxidants are given.

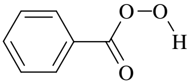
Oxygen

See Oxygen (Gas): Benzoic acid

See other ORGANIC ACIDS

2729. Peroxybenzoic acid

[93-59-4] **$C_7H_6O_3$**



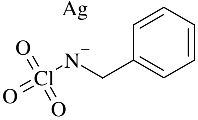
1. Baeyer, A. *et al., Ber.*, 1900, **33**, 1577
2. Silbert, L. S. *et al., Org. Synth.*, 1963, **43**, 95

It explodes weakly on heating [1]. A chloroform solution of peroxybenzoic acid exploded during evaporation of solvent. Evaporation should be avoided or conducted with full precautions [2].

See other PEROXYACIDS

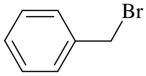
2730. Silver *N*-perchlorylbenzylamide

[89521-43-7] **$C_7H_7AgClNO_3$**



Hennrichs, W. *et al., Z. Anorg. Chem.*, 1983, **506**, 203—207
It explodes on impact or on heating above 105°C.
See entry PERCHLORYLAMIDE SALTS (reference 2)
See other N-METAL DERIVATIVES, SILVER COMPOUNDS

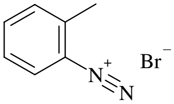
2731. Benzyl bromide
[100-39-0] **C_7H_7Br**



HCS 1980, 200

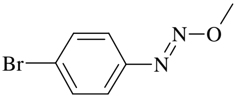
Molecular sieve
Harris, T. D., *Chem. Eng. News*, 1979, **57**(12), 74
Redistilled bromide was stored over 4A molecular sieve previously activated at 300°C. After 8 days the closed bottle burst from internal pressure of hydrogen bromide. This was attributed to the sieve catalysing a Friedel-Craft type intermolecular condensation-polymerisation with liberation of hydrogen bromide.
Benzyl alcohol: Hydrogen bromide, Iron
See Benzyl chloride: Catalytic impurities
See other BENZYL COMPOUNDS, GAS EVOLUTION INCIDENTS, MOLECULAR SIEVE INCIDENTS, POLYCONDENSATION REACTION INCIDENTS

2732. 2-Toluenediazonium bromide
[54514-12-4] **$C_7H_7BrN_2$**



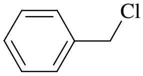
Copper powder
Vogel, 1956, 606—607
During the decomposition of the diazonium solution by warming with copper bronze to give 2-bromotoluene, strong cooling must be applied immediately to prevent the nitrogen evolution becoming violent and ejecting the flask contents.
See other DIAZONIUM SALTS, GAS EVOLUTION INCIDENTS

2733. Methyl 4-bromobenzenediazoate
[67880-26-6] **$C_7H_7BrN_2O$**



Bamberger, E., *Ber.*, 1895, **28**, 233
It explodes on heating.
See other ARENEDIAZOATES, N—O COMPOUNDS

2734. Benzyl chloride
[100-44-7] **C_7H_7Cl**



HCS 1980, 202

Oehme, F., *Chem. Tech.* (Berlin), 1952, **4**, 404
During distillation of the technical chloride, hydrogen chloride was evolved, air was bubbled through to remove it, and there was an explosion. This was attributed to a polycondensation (intermolecular Friedel-Craft) reaction, possibly catalysed by oxidation products.

Energy of decomposition (in range 290—370°C) measured as 0.14 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Catalytic impurities
Naef, H., private comm., 1980
The chloride is usually (but not always) stabilised in storage by addition of aqueous alkali or anhydrous amines as acid acceptors. A 270 kg batch which was not stabilised polymerised violently when charged into a reactor. Contact of the chloride (slightly hydrolysed and acidic) with rust led to formation of ferric chloride which catalysed an intermolecular Friedel-Craft reaction to form polybenzyls with evolution of further hydrogen chloride. Contact of unstabilised benzyl chloride with aluminium, iron or rust should be avoided to obviate the risk of polycondensation.
Benzyl alcohol: Hydrogen bromide, Iron
1,2-Bis(chloromethyl)benzene: Catalytic impurities
See Benzyl bromide: Molecular sieve
See other GAS EVOLUTION INCIDENTS, POLYCONDENSATION REACTION INCIDENTS

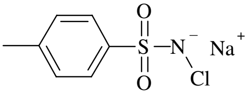
Other reactants
Yoshida, 1980, 331
MRH values for 13 combinations with oxidants are given, many values being high.

Sodium acetate, Pyridine
Bast, —, *Proc. 1st Int. Symp. Prev. Occ. Risks Chem. Ind.*, 194—199, Heidelberg, ISSA, 1970
Benzyl acetate was prepared by addition of benzyl chloride (containing 0.6% pyridine as stabiliser) to preformed sodium acetate at 70°, followed by heating at 115°, then finally up to 135°C to complete the reaction. On one occasion, gas began to be evolved at the end of the dehydration phase, and the reaction accelerated to a violent explosion, rupturing the 25 mm thick cast iron vessel. This was attributed to presence of insufficient pyridine to maintain basicity, dissolution of iron by the acidic mixture, and catalysis by ferric chloride of a Friedel-Craft type polycondensation reaction to polybenzyls, with evolution of hydrogen chloride, which at 130°C would produce an overpressure approaching 100 bar. Previously the chloride had been supplied in steel drums containing 10% sodium carbonate or 3% sodium hydroxide solutions as

stabilisers, but the packing was changed to polythene-lined kegs and the stabiliser omitted. However, higher pyridine concentrations effectively stabilise the chloride in steel drums.
See Catalytic impurities, above

Sodium cyanide
Nolan, 1983, Case history 192
Benzyl cyanide was prepared from the chloride and sodium cyanide in aqueous methanol. Inadequate cooling of the reactor led to a fire.
See other BENZYL COMPOUNDS, GAS EVOLUTION INCIDENTS, POLYCONDENSATION REACTION INCIDENTS

2735. Sodium *N*-chloro-4-toluenesulfonamide
[127-65-1] **$C_7H_7ClNNaO_2S$**



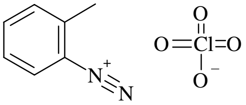
1. Klundt, I. L., *Chem. Eng. News*, 1977, **55**(49), 56
2. Kirk Othmer, (4th Edn), 1993, Vol IV, 921

The anhydrous salt (‘Chloramine-T’) explodes at 175°C, but a small quantity exploded after storage in a bottle at ambient temperature [1]. The trihydrate may explode as low as 130°C, the anhydrous compound is less stable still [2].

Calcium carbonate, Isonitriles
Sorbe, 1968, 137
Mixtures explode when warmed on the steam-bath in presence of calcium carbonate.

Isonitriles, Anthranilates, Tetraethylammonium chloride
Bossio, R. *et al., J. Heterocycl. Chem.*, 1995, **32**(4), 1115
A one pot synthesis of heterocycles involving the above reagents and catalyst sometimes showed an induction period followed by violent reaction.
See other N-HALOGEN COMPOUNDS

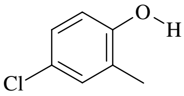
2736. 2-Toluenediazonium perchlorate
[68597-04-6] **$C_7H_7ClN_2O_4$**



Hofmann, K. A. *et al., Ber.*, 1906, **39**, 3146
The solid salt is explosive even when wet.
See other DIAZONIUM PERCHLORATES

2737. 4-Chloro-2-methylphenol

[1570-64-5] **C_7H_7ClO**



Sodium hydroxide

Anon., *ABCM Quart. Safety Summ.*, 1957, **28**, 39

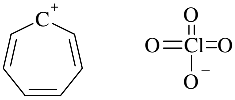
A large quantity (700 kg) of the chlorophenol, left in contact with conc. sodium hydroxide solution for 3 days, decomposed, attaining red heat and evolving fumes which ignited explosively. Although this could not be reproduced under laboratory conditions, it is believed that exothermic hydrolysis to the hydroquinone (possibly with subsequent aerobic oxidation to the quinone) occurred, the high viscosity of the liquid preventing dissipation of heat.

See Sodium 4-chloro-2-methylphenoxide

See other HALOARYL COMPOUNDS

2738. Tropylium perchlorate

[25230-72-2] **$C_7H_7ClO_4$**



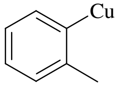
1. Ferrini, P. G. *et al., Angew. Chem.*, 1962, **74**, 488
2. Barltrop, J., *Chem. Brit.*, 1980, **16**, 452

Pressing the salt through a funnel with a glass rod caused a violent explosion [1], and grinding 19 g of the dry salt in a mortar led to the same result.

See other NON-METAL PERCHLORATES

2739. 2-Tolylcopper

[20854-03-9] **C_7H_7Cu**



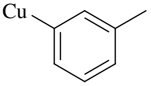
Camus, A. *et al., J. Organomet. Chem.*, 1968, **14**, 442—443

The solid 2- isomer usually exploded strongly on exposure to oxygen at 0°C, or weakly on heating above 100°C under vacuum.

See other ARYLMETALS

2741. 3-Tolylcopper

[20854-05-1] **C_7H_7Cu**



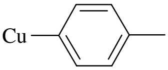
Camus, A. *et al., J. Organomet. Chem.*, 1968, **14**, 442—443

The solid 3- isomers usually exploded strongly on exposure to oxygen at 0°C, or weakly on heating above 100°C under vacuum.

See other ARYLMETALS

2742a. 4-Tolylcopper

[5588-74-9] **C_7H_7Cu**



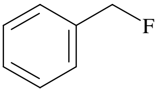
Camus, A. *et al., J. Organomet. Chem.*, 1968, **14**, 442—443

The solid 4- isomers usually exploded strongly on exposure to oxygen at 0°C, or weakly on heating above 100°C under vacuum.

See other ARYLMETALS

2742b. Benzyl fluoride (α-Fluorotoluene)

[25496-08-6] **C_7H_7F**



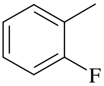
Szucs, S. S., *Chem. Eng. News.*, 1990 **68**(34), 2

A bottle exploded on storage, coating the surroundings with polymer. It is considered that glass has catalytic properties for the Friedel Crafts polymerisation reaction.

See other BENZYL COMPOUNDS, POLYCONDENSATION REACTION INCIDENTS

†2743. 2-Fluorotoluene

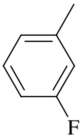
[952-52-3] **C_7H_7F**



See other HALOARYL COMPOUNDS

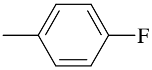
†2744. 3-Fluorotoluene

[352-70-5] **C_7H_7F**



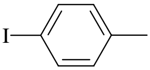
See other HALOARYL COMPOUNDS

†2745. 4-Fluorotoluene
[352-32-9] **C_7H_7F**



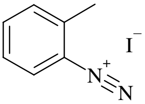
See other HALOARYL COMPOUNDS

2746. 4-Iodotoluene
[624-31-7] **C_7H_7I**



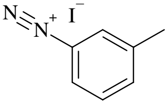
Sorbe, 1968, 66
It explodes above 200°C.
See other HALOARYL COMPOUNDS, IODINE COMPOUNDS

2747. 2-Toluenediazonium iodide
[54514-15-7] **$C_7H_7IN_2$**



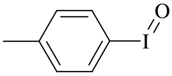
See 3-Toluenediazonium salts,
See also DIAZONIUM TRIIODIDES
See other DIAZONIUM SALTS

2748. 3-Toluenediazonium iodide
[54514-15-7] **$C_7H_7IN_2$**



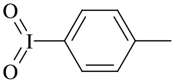
See 3-Toluenediazonium salts,
See also DIAZONIUM TRIIODIDES
See other DIAZONIUM SALTS

2749. 4-Iodosyltoluene
[69180-59-2] **C_7H_7IO**



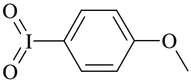
Sorbe, 1968, 66
It explodes at above 175°C
See other IODINE COMPOUNDS

2750. 4-Iodyltoluene
[16825-72-2] **$C_7H_7IO_2$**



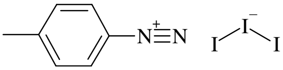
Sorbe, 1968, 66
It explodes at above 200°C.
See other IODINE COMPOUNDS

2751. 4-Iodylanisole
[16825-74-4] **$C_7H_7IO_3$**



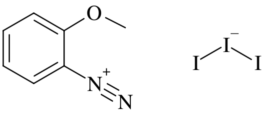
Leymann, —, *Chem. Fabrik.*, 1928, 705
A 1.5 kg quantity of pure material, prepared as a disinfectant, exploded with great violence when a door was opened, possibly during drying operations. It explodes at 225°C.
See other IODINE COMPOUNDS

2752. 4-Toluenediazonium triiodide
[68596-94-1] **$C_7H_7I_3N_2$**



See entry DIAZONIUM TRIIODIDES

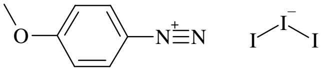
2753. 2-Methoxybenzenediazonium triiodide
[68596-92-9] **$C_7H_7I_3NO$**



See entry DIAZONIUM TRIIODIDES

2754. 2-Methoxybenzenediazonium triiodide

[68596-91-8] **$C_7H_7I_3NO$**



See entry DIAZONIUM TRIIODIDES

2755. Vinylpyridine

[1337-81-1] **C_7H_7N**

Aminium nitrites

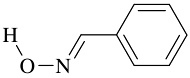
Karakuleva, G. I. *et al.*, Russ. Pat. 396 349, 1973

Nitrite salts inhibit the sometimes explosive spontaneous polymerisation of '*N*-vinylpyridine derivatives'.

See other ORGANIC BASES, POLYMERISATION INCIDENTS

2756. Benzaldehyde oxime

[932-90-1] **C_7H_7NO**



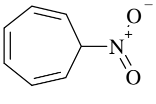
Energy of decomposition (in range 160—350°C) measured as 1.37 kJ/g by DSC, and T_{ait24} was determined as 108°C by adiabatic Dewar tests, with an apparent energy of activation of 96 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other OXIMES

2757. 1-Nitrocyclohepta-1,3,5-triene

[156545-33-4] **$C_7H_7NO_2$**



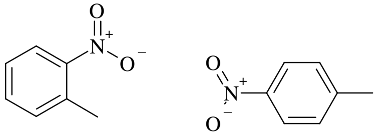
Burnett, I. J. *et al., J. Chem. Soc., Chem Comm.*, 1994, (10) 1187.

This compound can decompose explosively if stored at room temperature.

See other *C*-NITRO COMPOUNDS

2758. *mixo*-Nitrotoluene

[1321-12-6] **$C_7H_7NO_2$**

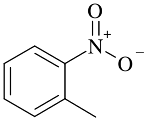


1. Staudinger, H., *Z. Angew. Chem.*, 1922, **35**, 657—659
2. Harris, G. F. P. *et al., Runaway Reactions*, 1981, Paper 4/W, 1—11
3. Anon., *Euro. Chem. News*, 1992, 3558(1548), 27; *ibid.*, 1993, **59**(1562), 22; *Chem. Brit.*, 1993, **29**(1), 15
4. Anon., *Chem. & Ind.*, 1994, 485
5. *The Fire at Hickson and Welch Ltd.*, HSE Books, Sudbury UK, 1994
6. Todd, J. et al., *International Conference on 20 th Anniversary of the Bhopal Gas Tragedy*, 2004, Paper 70
7. U.S. Chemical Safety and Hazard Investigation Board, Report 2003-01-1-MS

The combined residues (300—400 kg) from several vacuum distillations at up to 180°C/40 mbar of a mixture of the 2- and 4-isomers exploded several hours after distillation had been completed. It appeared probable that admission of air to cool the hot residue initiated autoxidative heating, possibly involving nitrogen oxide and catalysis by iron, which eventually led to explosion of the residue, which probably contained polynitro compounds [1]. Explosions have occurred during fractional distillation to separate mixed nitrotoluene isomers when excessive heating was employed, or when the materials were held at more moderate temperatures but for long periods. The factors involved were identified by a series of systematic thermal stability tests on various mixtures, some including dinitrotoluenes. It was established that decomposition would not occur on the large scale if still temperatures were limited to 190°C [2]. An explosion occurred, killing five workers, when raking out (with metal rakes) the 40 cm accumulated residues from thirty years nitrotoluene distillations. It appears to have been initiated by runaway decomposition from hot-spots developed when a steam coil, possibly at 165°C, was used to soften the still tars, which were not in contact with the thermocouple, by heating to a specified 80°C. There is a suggestion that nitrocresol byproducts were involved [3,4]. A full report on this event has been published [5]. In a possibly similar accident, a distillation column, contaminated with unidentified 'foulant' exploded after a prolonged period on stand-by, starting at 161°C. It was hypothesised that air leakage formed nitrocresol, simultaneously raising the temperature to >200°C [6]. An earlier, and authoritative, report on what seems the same incident found no need to invoke foulant or nitrocresol, finding that the feedstock itself showed self-heating to runaway from probable start temperature over suitable time-periods. A passing steam valve is suggested as the cause of the initial temperature rise [7].

See other NITROARYL COMPOUNDS

2759. 2-Nitrotoluene
[88-72-2] **$C_7H_7NO_2$**



HCS 1980, 690

T_{ait24} was determined as 232°C by adiabatic Dewar tests, with an apparent energy of activation of 162 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkali

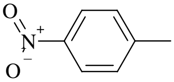
1. Anon., *Loss Prev. Bull.*, 1977, (013), 2
2. Hauptli, H., private comm., 1976

1,2-Bis(2-nitrophenyl)ethane (2,2'-dinitrobibenzyl) is prepared industrially by action of alkali on 2-nitrotoluene, and the highly exothermic reaction is controlled by the rate of addition of the nitro compound to the other cooled reaction components, to keep the temperature at 5—10°C. During one batch, failure of the agitator caused increase in temperature and at 15° the temperature monitor stopped addition of nitrotoluene and increased cooling, the temperature rose to 20° and the building was evacuated. After the exotherm had subsided, the agitator was used very intermittently to assist cooling and mixing. At 12°C full agitation was restored and processing continued to completion [1]. Similar caution is necessary during the preparation of other analogous nitrobibenzyls [2].
See other AGITATION INCIDENTS

Sodium hydroxide

Anon., *ABCM Quart. Safety Summ.*, 1945, **16**, 2
Crude 2-nitrotoluene, containing some hydrochloric and acetic acids, was charged into a vacuum still with flake sodium hydroxide to effect neutralisation prior to distillation. An explosion occurred later. Similar treatments had been used uneventfully previously, using the weaker bases lime or sodium carbonate for neutralisation. It seems likely that the explosion involved formation and violent decomposition of the sodium salt of an *aci*-nitro species, possibly of quinonoid type.
See aci-NITROQUINONOID COMPOUNDS, NITROAROMATIC—ALKALI HAZARDS
See other NITROARYL COMPOUNDS

2760. 4-Nitrotoluene
[99-99-0] **$C_7H_7NO_2$**



HCS 1980, 691

1. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
2. Widmann, G. *et al., Thermochim. Acta*, 1988, **134**, 451—455
3. Anon., *ABCM Quart. Safety Summ.*, 1938, **9**, 65; 1939, **10**, 2

Energy of decomposition (in range 300—420°C) was measured as 1.74 kJ/g by DSC, and T_{ait24} was determined as 232°C by adiabatic Dewar tests, with an apparent energy of activation of 162 kJ/mol [1]. Energy of decomposition of pure 4-nitrotoluene in the range 240—460°C was determined by micro DSC as 3.52 kJ/g, peaking at 409°C [2]. The residue from large-scale vacuum distillation of 4-nitrotoluene was left to cool after turning off heat and vacuum, and after 8 h a violent explosion occurred. This was variously attributed to: presence of an excessive proportion of dinitrotoluenes in the residue, which would decompose on prolonged heating; presence of traces of alkali in the crude material, which would form unstable *aci*-nitro salts during distillation; ingress of air to the hot residue on shutting off the vacuum supply, and subsequent accelerating oxidation of the residue. All these factors may have contributed, and several such incidents have occurred [3].

Sodium

Schmidt, J., *Ber.*, 1899, **32**, 2920

One of the products of treating 4-nitrotoluene in ether with sodium is a dark brown sodium derivative which ignites in air.

See also NITROAROMATIC—ALKALI HAZARDS

Sulfuric acid

1. Hunt, J. K., *Chem. Eng. News*, 1949, **27**, 2504
2. Chem. Abs., 1949, **43**, 8681a
3. McKeand, G., private comm., 1974
4. McKeand, G., *Chem. & Ind.*, 1974, 425

Solutions of 4-nitrotoluene in 93% sulfuric acid decompose very violently if heated to 160°C. This happened on plant-scale when automatic temperature control failed [1], but the temperature was erroneously abstracted as 135°C [2]. The explosion temperature of 160°C for the mixture (presumably containing a high proportion of 4-nitrotoluene-2-sulfonic acid) is 22°C lower than that observed for onset of decomposition when 4-nitrotoluene and 93% sulfuric acid are heated at a rate of 100°C/h [3]. Mixtures of 4-nitrotoluene with 98% acid or 20% oleum begin to decompose at 180 and 190°C, respectively [3][4]. Thereafter, decomposition accelerates (190—224° in 14 min, 224—270 in 1.5 min) until eruption occurs with evolution of much gas [4].

See also 3-Nitrobenzenesulfonic acid: Sulfuric acid

Sulfuric acid, Sulfur trioxide

Vervalin, H. C., *Hydrocarbon Process.*, 1976, **55**(9), 323

During sulfonation of 4-nitrotoluene at 32°C with 24% oleum in a 2000 l vessel, a runaway decomposition reaction set in and ejected the contents as a carbonaceous mass. The thermal decomposition temperature was subsequently estimated as 52°C (but see above).

See other SULFONATION INCIDENTS

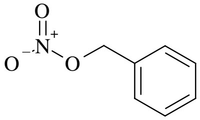
Tetranitromethane

See Tetranitromethane: Aromatic nitro compounds

See other NITROARYL COMPOUNDS

2761. Benzyl nitrate

[15285-42-4] **$C_7N_7NO_3$**



1. Nef, J. U., *Ann.*, 1899, **309**, 172
2. Verbal comment on presentation by Verhoeff, J., *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C5—13, Rugby, IChE, 1983

It decomposed explosively at 180—200°C [1], but there is a pressure band between ambient and 64 bar in which thermal explosion does not occur [2].

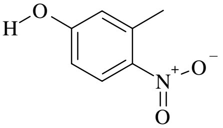
Lewis acids

See entry ALKYL NITRATES

See other BENZYL COMPOUNDS

2762. 3-Methyl-4-nitrophenol

[2581-34-2] **$C_7H_7NO_3$**



Dartnell, R. C. *et al., Loss Prev.*, 1971, **5**, 53—56; *MCA Case History No. 1649*

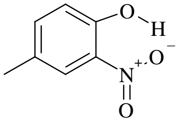
A batch of 8 t of material accumulated in storage at 154°C during 72 h decomposed explosively. Stability tests showed that thermal instability developed when 3-methyl-4-nitrophenol is stored molten at temperatures above 140°C. Decomposition set in after 14 h at 185° or 45 h at 165°, with peak temperatures of 593 and 521°C, respectively. In a closed vessel, a peak pressure of 750 bar was attained, with a maximum rate of increase of 40 kbar/s. Thermal degradation involves an initially slow exothermic free radical polymerisation process, followed by a rapid and violently exothermic decomposition at take-off.

See THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

See other NITROARYL COMPOUNDS

2763. 4-Methyl-2-nitrophenol
[119-33-5] **$C_7H_7NO_3$**



Sodium hydroxide, Sodium carbonate, Methanol

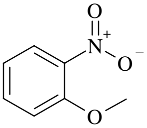
MCA Case History No. 701

Failure to agitate a large-scale mixture of the reagents caused an eruption owing to action of the exotherm when mixing did occur.

See entry NITROAROMATIC—ALKALI HAZARDS

See other AGITATION INCIDENTS

2764. 2-Nitroanisole
[91-23-6] **$C_7H_7NO_3$**



Hydrogen

1. Carswell, T. S., *J. Amer. Chem. Soc.*, 1931, **53**, 2417
2. Adkins, H., *J. Amer. Chem. Soc.*, 1931, **53**, 2808

Catalytic hydrogenation on 400 g scale at 34 bar under excessively vigorous conditions (250°C, 12% catalyst, no solvent) caused the thin autoclave without bursting disk to rupture [1]. Under more appropriate conditions the hydrogenation is safe [2].

See other CATALYTIC NITRO REDUCTION PROCESSES

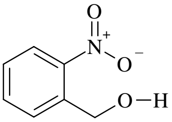
Sodium hydroxide, Zinc

Anon., *Angew. Chem. (Nachr.)*, 1955, **3**, 186

In the preparation of 2,2’-dimethoxyazoxybenzene, solvent ethanol was distilled out of the mixture of 2-nitroanisole, zinc and sodium hydroxide before reaction was complete. The exothermic reaction continued unmoderated, and finally exploded.

See other NITROAROMATIC—ALKALI HAZARDS, NITROARYL COMPOUNDS

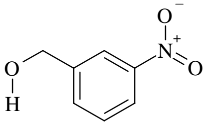
2765. 2-Nitrobenzyl alcohol
[612-25-9] **$C_7N_7NO_3$**



See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2766. 3-Nitrobenzyl alcohol

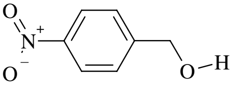
[619-25-0] **$C_7H_7NO_3$**



See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2767. 4-Nitrobenzyl alcohol

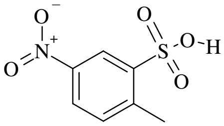
[619-73-8] **$C_7H_7NO_3$**



See entry NITROBENZYL COMPOUNDS (reference 3)
See other BENZYL COMPOUNDS, NITROARYL COMPOUNDS

2768. 2-Methyl-5-nitrobenzenesulfonic acid

[121-03-9] **$C_7H_7NO_5S$**

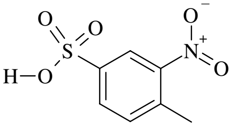


Preparative hazard

See 4-Nitrotoluene: Sulfuric acid, or : Sulfuric acid, Sulfur trioxide
See other NITROARYL COMPOUNDS, ORGANIC ACIDS

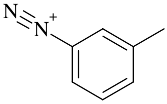
2769. 4-Methyl-3-nitrobenzenesulfonic acid

[97-06-3] **$C_7H_7NO_5S$**



Hakl, J., *Runaway Reactions*, 1981, paper 3/L, 5
Initial exothermic decomposition sets in at 170°C.
See other NITROARYL COMPOUNDS, ORGANIC ACIDS

2770. 3-Toluenediazonium salts
[14604-29-6] (ion) **$C_7H_7N_2^+ Z^-$**



Potassium iodide

Trumbull, E. R., *J. Chem. Educ.*, 1971, **48**, 640

Addition of potassium iodide solution to diazotised 3-toluidine was accommpanied on 3 occasions by an eruption of the beaker contents. This was not observed with the 2- and 4-isomers or other aniline derivatives.

See DIAZONIUM TRIIODIDES
See other DIAZONIUM SALTS

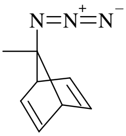
Potassium *O*-ethyl dithiocarbonate

1. Tarbell, D. S. *et al., Org. Synth.*, 1955, Coll. Vol. 3, 810
2. Parham, W. E. *et al., Org. Synth.*, 1967, **47**, 107; Coll. Vol. V, 1050
3. Editor's comment

During interaction of the diazonium chloride, and the *o*-ethyl dithiocarbonate ('xanthate') solutions, care must be taken to ensure that the intermediate diazonium dithiocarbonate decomposes to 2-thiocresol as fast as it is formed [1]. This can be assured by presence of a trace of nickel in the solution to effect immediate catalytic decomposition. When the 2 solutions were mixed cold and then heated to effect decomposition, a violent explosion occurred [2]. Caution: The experiments claimed to show catalysis by nickel appear to have been performed on diazotised anthranilic acid; which is the only benzenediazonium system never known to give explosive intermediates with sulfur nucleophiles [3].

See other DIAZONIUM SULFIDES AND DERIVATIVES

2773. 7-Azidobicyclo[2.2.1]hepta-2,5-diene
[104172-76-1] **$C_7H_7N_3$**

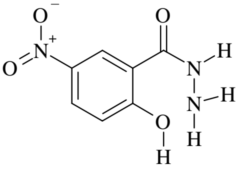


Hoffmann, R. W. *et al., Chem. Ber.*, 1986, **119**, 3309

It is explosive, and when distilled at 41°C/1.3 mbar, the bath temperature must not exceed 100°C.
See other DIENES, ORGANIC AZIDES

2774. 5-Nitrosalicylhydrazide

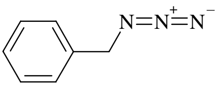
[946-32-7] **$C_7H_7N_3O_4$**



Khadikar, P. V. *et al., Thermochim Acta*, 1986, (99), 109—118
Several heavy metal complexes of the hydrazide ($ML_2 . 2H_2O$) exploded around 250°C during thermal analysis.
See other NITROARYL COMPOUNDS
See related HEAVY METAL DERIVATIVES

2775. Benzyl azide

[622-79-7] **$C_7N_7N_3$**

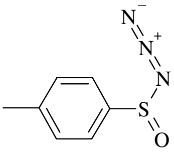


Sorbe, 1968, 138
A particularly heat-sensitive explosive oil.

Bis(trifluoromethyl) nitroxide
See Bis(trifluoromethyl) nitroxide: Benzoyl azide
See other BENZYL COMPOUNDS, ORGANIC AZIDES

2776. 4-Toluenesulfinyl azide

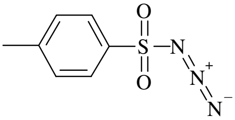
[40560-76-7] **$C_7H_7N_3OS$**



See entry SULFINYL AZIDES
See other ACYL AZIDES

2777. 4-Toluenesulfonyl azide

[941-55-9] **$C_7H_7N_3O_2S$**



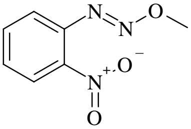
1. Rewicki, D. *et al., Angew. Chem. (Intern. Ed.)*, 1972, **11**, 44
2. Roush, W. R. *et al., Tetrahedron. Lett.*, 1974, 1391—1392
3. Spencer, H., *Chem. Brit.*, 1981, **17**, 106

The impure compound, present as a majority in the distillation residue from preparation of 1-diazoindene, will explode if the bath temperature exceeds 120°C [1]. A polymer-bound sulfonyl azide reagent has been described as safer in use than the title compound [2]. Distillation of the azide at 130—132°C/~0.5 mbar from an oil bath at 145°C led to darkening, then violent explosion of the 30—40% residue [3].

See other ACYL AZIDES

2778. Methyl 2-nitrobenzenediazoate

[62375-91-1] **$C_7H_7N_3O_3$**



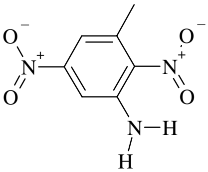
Bamberger, E., *Ber.*, 1895, **28**, 237

It explodes violently on heating, or on disturbing after 24 h confinement in a sealed tube at ambient temperature. The 4-nitro analogue is more stable.

See other ARENEDIAZOATES

2779. 3-Amino-2,5-dinitrotoluene

[65321-68-8] **$C_7H_7N_3O_4$**

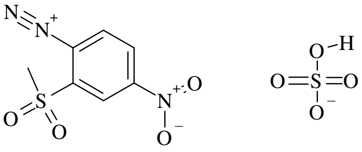


Preparative hazard

See 2,5-Dinitro-3-methylbenzoic acid: Oleum, Sodium azide

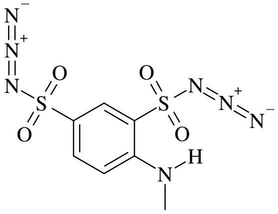
See other POLYNITROARYL COMPOUNDS

2780. 2-Methanesulfonyl-4-nitrobenzenediazonium hydrogen sulfate
[68597-08-0] **$C_7H_7N_3O_8S_2$**



See entry DIAZONIUM SULFATES

2781. 4-Methylaminobenzene-1,3-bis(sulfonyl azide)
[87425-02-3] **$C_7H_7N_7O_4S_2$**

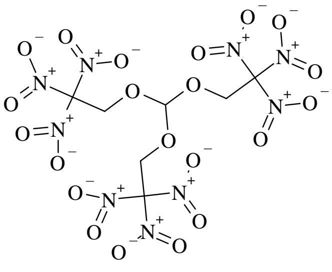


Lenox, R. S., US Pat. 4 393 006, 1983

It detonates on melting.

See other ACYL AZIDES

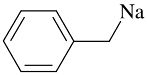
2782. Tris(2,2,2-trinitroethyl) orthoformate
[14548-59-5] **$C_7H_7N_9O_{21}$**



See entry TRINITROETHYL ORTHOESTERS

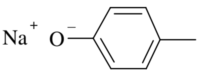
See other POLYNITROALKYL COMPOUNDS

2783. Benzylsodium
[1121-53-5] **C_7H_7Na**



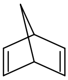
Leleu, *Cahiers*, 1977, (88), 370
It ignites in air.
See other BENZYL COMPOUNDS, ORGANOMETALLICS
See related ALKYLMETALS

2784. Sodium 4-methylphenoxide (Sodium 4-cresolate)
[22113-51-5] (ion) **C_7H_7NaO**



May & Baker Ltd, private comm., 1968
Sodium 4-methylphenoxide solution was dehydrated azeotropically with chlorobenzene, and the filtered solid was dried in an oven, where it soon ignited and glowed locally. This continued for 30 min after it was removed from the oven. A substituted potassium phenoxide, prepared differently, also ignited on heating. Finely divided and moist alkali phenoxides may be prone to vigorous oxidation (or perhaps reaction with carbon dioxide) when heated in air.

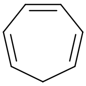
†2785. Bicyclo[2.2.1]hepta-2,5-diene
[121-46-0] **C_7H_8**



HCS 1980, 209

See related DIENES

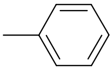
†2786. 1,3,5-Cycloheptatriene
[544-25-2] **C_7H_8**



HCS 1980, 341

See related DIENES

†2787. Toluene (Methylbenzene)
[108-88-3] **C_7H_8**



(*MCA SD-63*, 1956); *NSC 204*, 1968; *FPA H11*, 1973; *HCS 1980*, 906;
RSC Lab. Hazard Data Sheet No. 15, 1983

Other reactants

Yoshida, 1980, 261

MRH Values calculated for 15 combinations with oxidants are given.

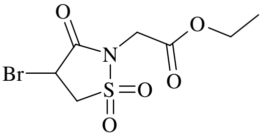
Oxidants	MRH values show % of oxidant
See Bromine trifluoride: Solvents	MRH 2.97/80
1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione: Xylene	
Dinitrogen tetraoxide: Hydrocarbons	MRH 7.15/81
Nitric acid: Hydrocarbons	MRH 6.07/82
Tetranitromethane: Hydrocarbons	
Uranium hexafluoride: Aromatic hydrocarbons	

Sulfur dichloride

See Sulfur dichloride: Toluene

2788. Ethyl 4-bromo-1,1,3-trioxoisothiazoleacetate

[126623-64-1] **$C_7H_8BrNO_5S$**



Ethyl diazoacetate

Burri, K. F., *Helv. Chim. Acta*, 1989, **72**(6), 1416

It is suggested that both adducts of these compounds are explosive.

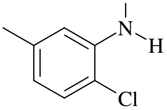
See Ethyl 6-ethoxycarbonyl-3,4-dihydro-1,1,3-trioxo-2-pyrazolo [3,4-d]isothiazole-2-acetate

See Ethyl diazoacetate

See other N—S COMPOUNDS

2789. 2-Chloro-5-methylaniline

[95-81-8] **C_7H_8ClN**



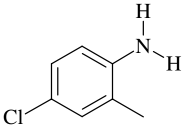
Preparative hazard

See 2-Chloro-5-methylphenylhydroxylamine

See other HALOANILINES

2790. 4-Chloro-2-methylaniline

[95-69-2] **C_7H_8ClN**



See 4-Chloro-2-methylbenzenediazonium salts

Copper(II) chloride

Kotoyori, T. *et al., J. Haz. Mat.*, 1976, 252—262

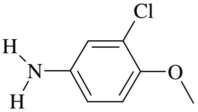
At the end of vacuum distillation of 4-chloro-2-methylaniline, the 1300 l still burst owing to internal gas pressure from an unexpected decompositon reaction. Subsequent investigation showed that copper(I) oxide present in the still charge would react with hydrogen chloride and air leaking in to produce copper(II) chloride. The latter is an effective catalyst for decomposition of the haloaniline at 239°C to produce hydrogen chloride. The physical conditions of the installation were compatible with this mechanism, and enough chloroaniline was present to exceed the bursting pressure of the vessel by a factor of 3. It is concluded that halogenated aromatic amines should be distilled under alkaline conditions in absence of air.

See CATALYTIC IMPURITY INCIDENTS

See other HALOANILINES

2791. 3-Chloro-4-methoxyaniline

[5345-54-0] **C_7H_8ClNO**



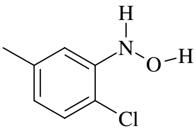
Heat of decomposition was determined as 0.82 kJ/g by DSC, and T_{ait24} was determined as 158°C by adiabatic Dewar tests, with an apparent energy of activation of 135 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other AMINOMETHOXY COMPOUNDS, HALOANILINES

2792. 2-Chloro-5-methylphenylhydroxylamine

[65039-20-5] **C_7H_8ClNO**



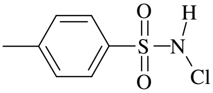
Rondevstedt, C. S., *Chem. Eng. News*, 1977, **55**(27), 38; *Synthesis*, 1977, 851—852

In an attempt to reduce 2-chloro-5-methylnitrobenzene to the aniline by treatment with excess hydrazine and Pd/C catalyst, the hydroxylamine was unexpectedly produced as major product. During isolation of the product, after removal of solvent it was heated to 120°C under vacuum and exploded fairly violently. Many arylhydroxylamines decompose violently when heated above 90—100°C, especially in presence of acids. GLC is not suitable as an analytical diagnostic for arylhydroxylamines because of this thermal decomposition.

See 3,4-Dichlorophenylhydroxylamine

See other CATALYTIC NITRO REDUCTION PROCESSES, N—O COMPOUNDS

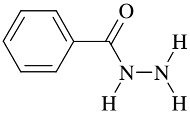
2793. *N*-Chlorotoluene-4-sulfonamide
[144-86-5] **$C_7H_8ClNO_2S$**



Energy of exothermic decomposition in range 110—330°C was measured as 1.36 kJ/g/

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

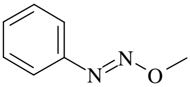
2794. Benzohydrazide
[613-94-5] **$C_7H_8N_2O$**



Benzeneseleninic acid

See Benzeneseleninic acid: Hydrazine derivatives

2795. Methyl benzenediazoate (1-Phenyl-2-methoxydiazene)
[66217-76-3] **$C_7H_8N_2O$**

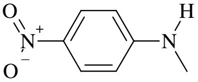


Bamberger, E., *Ber.*, 1895, **28**, 228

It explodes on heating or after storage for 1 h in a sealed tube at ambient temperature.

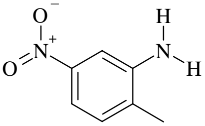
See other ARENEDIAZOATES

2796. *N*-Methyl-4-nitroaniline
[100-15-2] **$C_7H_8N_2O_2$**



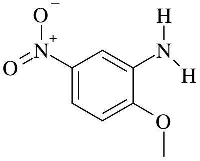
2,4-Dithia-1,3-dioxane-2,2,4,4-tetraoxide (‘Carbyl sulfate’)
See 2,4-Dithia-1,3-dioxane-2,2,4,4-tetraoxide: *N*-Methyl-4-nitroaniline
See other NITROARYL COMPOUNDS

2797. 2-Methyl-5-nitroaniline
[99-55-8] **$C_7H_8N_2O_2$**



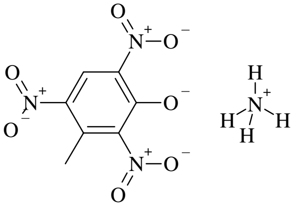
Hakl, J., *Runaway Reactions*, 1981, Paper 3/L, 5
Initial exothermic decomposition sets in at 150°C.
See other NITROARYL COMPOUNDS

2798. 2-Methoxy-5-nitroaniline
[99-59-2] **$C_7H_8N_2O_3$**



Preparative hazard
See 2-Methoxyanilinium nitrate: Sulfuric acid
See other AMINOMETHOXY COMPOUNDS, NITROARYL COMPOUNDS

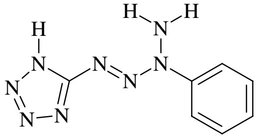
2799. Ammonium 3-methyl-2,4,6-trinitrophenoxide
[58696-86-9] **$C_7H_8N_4O_7$**



Biasutti, 1981, 63
An old store of the explosive material exploded violently with no apparent cause. A similar incident had been recorded previously. Some isomeric *aci*-nitroquinonoid salt may have been formed.
See aci-NITROQUINONOID COMPOUNDS
See other POLYNITROARYL COMPOUNDS

2800. 3-Phenyl-1-(5-tetrazolyl)-1-tetrazene

[ ] $C_7H_8N_8$



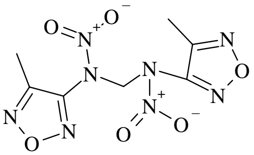
Thiele, J., *Ann.*, 1892, **270**, 60

It explodes on warming, as do *C*-substituted homologues.

See other HIGH-NITROGEN COMPOUNDS, TETRAZENES, TETRAZOLES

2801. Methylenebis(3-nitramino-4-methylfurazan)

[ ] $C_7H_8N_8O_6$



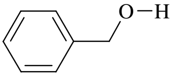
Willer, R. L. *et al., J. Heterocycl. Chem.,* 1992, **29**(7), 1835

An explosive of moderate sensitivity, thermally decomposing (non-explosively) from 120°C. The 4-nitro analogue was also explosive and decomposed from 90°C.

See other HIGH-NITROGEN COMPOUNDS, N—NITRO COMPOUNDS

2802. Benzyl alcohol

[100-51-6] C_7H_8O



HCS 1980, 198

Hydrogen bromide, Iron

Iselin, E. *et al., Chem. Ing. Tech.*, 1972, **44**, 462

Benzyl alcohol contaminated with 1.4% of hydrogen bromide and 1.1% of dissolved iron(II) polymerises exothermally above 100°C. Bases inhibit the polymerisation reaction. In a laboratory test, alcohol containing 1% of HBr and 0.04% of Fe polymerised at about 150° with an exotherm to 240°C. Formation and iron-catalysed poly-condensation of benzyl bromide seems to have been implicated.

See Benzyl bromide: Molecular sieve, or : Catalytic impurities

See other BENZYL COMPOUNDS, POLYCONDENSATION REACTION INCIDENTS

Other reactants

Yoshida, 1980, 329

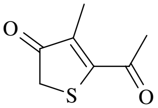
MRH values calculated for 13 combinations with oxidants are given.

Sulfuric acid MRH 1.13/48

See Sulfuric acid: Benzyl alcohol

2803. 2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one

[ ] **$C_7H_8O_2S$**



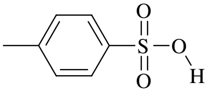
MCA Guide, 1972, 307

An explosion occurred during vacuum distillation. The highly conjugated compound could have been susceptible to peroxidation as well as capable of condensative polymerisation.

See other PEROXIDATION INCIDENTS, POLYCONDENSATION REACTION INCIDENTS

2804a. 4-Toluenesulfonic acid

[104-15-4] **$C_7H_8O_3S$**



HCS 1980, 908

Acetic anhydride, Water

See Acetic anhydride: 4-Toluenesulfonic acid, etc.

See other ORGANIC ACIDS

2804b. Thioanisole (Methylthiobenzene)

[ ] **C_7H_8S**

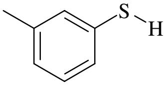
PhSMe

Nitric acid

See Nitric acid: Sulfuric acid, thioanisole

2805. 3-Thiocresol

[108-40-7] **C_7H_8S**

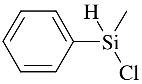


Preparative hazard

See 3-Toluenediazonium salts: Potassium *O*-ethyl dithiocarbonate

2806. Chloromethylphenylsilane

[1631-82-9] **C_7H_9ClSi**



4-Bromobutene, Chloroplatinic acid

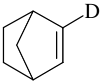
Brook, A. G. *et al., J. Organomet. Chem.*, 1975, **87**, 265

Interaction of chloromethylphenylsilane and 4-bromobutene, catalysed by chloroplatinic acid at 100°C, is extremely exothermic (to 165°C) and is accompanied by vigorous frothing.

See other ALKYLHALOSILANES

2807. 2-Deuterobicyclo[2.2.1]hept-2-ene

[694-94-0] **C_7H_9D**



Preparative hazard

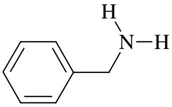
Shackelford, S. A., *Tetrahedron Lett.*, 1977, 4268, note 12

The metallation reaction involved in the preparation proved hazardous and unpredictable.

See related ALKENES

2808. Benzylamine

[100-46-9] **C_7H_9N**



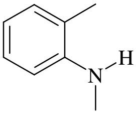
N-Chlorosuccinimide

See N-HALOIMIDES: Alcohols etc.

See other BENZYL COMPOUNDS, ORGANIC BASES

2809. 2-Toluidine

[95-53-4] **C_7H_9N**



HCS 1980, 910

Nitric acid MRH 6.11/81

See Nitric acid: Aromatic amines

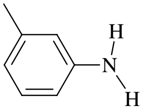
Other reactants

Yoshida, 1980, 260

MRH values calculated for 13 combinations with oxidants are given.

2810. 3-Toluidine

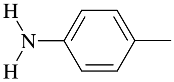
[108-44-1] **C_7H_9N**



See 3-Toluenediazonium salts

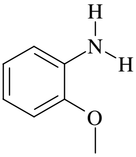
2811. 4-Toluidine

[106-49-0] **C_7H_9N**



2812. 2-Methoxyaniline (*o*-Anisidine)

[90-04-0] **C_7H_9NO**



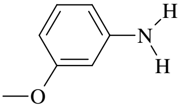
Energy of decomposition (in range 190—480°C) measured as 0.387 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other AMINOMETHOXY COMPOUNDS

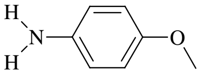
2813. 3-Methoxyaniline (*m*-Anisidine)

[536-90-3] **C_7H_9NO**



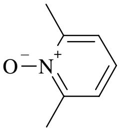
Energy of decomposition (in range 410—500°C) measured as 0.518 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AMINOMETHOXY COMPOUNDS

2814. 4-Methoxyaniline (*p*-Anisidine)
[104-94-9] **C_7H_9NO**



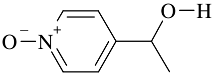
Energy of decomposition (in range 340—490°C) measured as 0.429 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AMINOMETHOXY COMPOUNDS

2815. 2,6-Dimethylpyridine *N*-oxide
[1073-23-0] **C_7H_9NO**



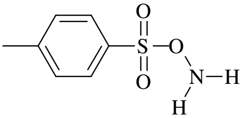
Phosphoryl chloride
See Phosphoryl chloride: 2,6-Dimethylpyridine *N*-oxide
See other N-OXIDES

2816. 4(1-Hydroxyethyl)pyridine *N*-oxide
[34277-48-0] **$C_7H_9NO_2$**



Taylor, R., *J. Chem. Soc., Perkin Trans. 2*, 1975, 279
The compound exploded during vacuum distillation, possibly owing to the presence of traces of peracetic acid.
See other N-OXIDES

2817. *O*-4-Toluenesulfonylhydroxylamine
[52913-14-1] **$C_7H_9NO_3S$**



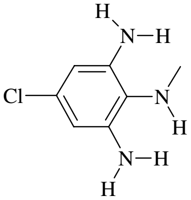
Carpino, L. A., *J. Amer. Chem. Soc.*, 1960, **82**, 3134

It deflagrated spontaneously on attempted isolation and drying at ambient temperature.

See O-Mesitylenesulfonylhydroxylamine

See other N—O COMPOUNDS

2818. 4-Chloro-2,6-diamino-*N*-methylaniline
[48114-68-7] **$C_7H_{10}ClN_3$**

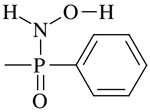


T_{ait24} determined as 148°C in adiabatic Dewar tests with apparent energy of activation of 123 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other HALOANILINES

2819. *N*-(Methylphenylphosphinoyl)hydroxylamine (*N*-Hydroxy-*P*-methyl-*P*-phenylphosphinamide)
[94193-56-3] **$C_7H_{10}NO_2P$**



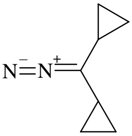
Harger, M. J. P., *J. Chem. Soc., Perkin Trans. 1*, 1987, 685

A sample decomposed vigorously after several hours at warm ambient temperature. The ethyl and isopropyl homologues appeared stable, but all (including the derived *O*-sulfonic acids) were treated as potentially unstable and were only heated briefly during crystallisation, and were stored at —20°C.

See other N—O COMPOUNDS

See related HYDROXYLAMINIUM SALTS

2820. Dicyclopropyldiazomethane
[16102-24-2] **$C_7H_{10}N_2$**



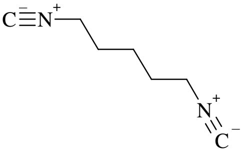
Ensslin, H. M *et al., Angew. Chem. (Intern. Ed.)*, 1967, **6**, 702—703

Storable in ether at —50°C, but violent decomposition of undiluted material sets in at —15°C.

See other DIAZO COMPOUNDS, STRAINED-RING COMPOUNDS

2821. 1,5-Diisocyanopentane

[97850-58-3] **$C_7H_{10}N_2$**

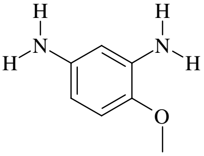


See entry DIISOCYANIDE LIGANDS

See related CYANO COMPOUNDS

2822. 4-Methoxy-1,3-phenylenediamine

[615-05-4] **$C_7H_{10}N_2O$**



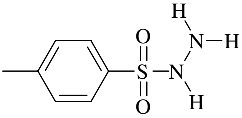
Energy of decomposition (in range 260—420°C) measured as 0.42 kJ/g by DSC, and T_{ait24} was determined as 207°C by adiabatic Dewar tests, with an apparent energy of activation of 114 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other AMINOMETHOXY COMPOUNDS

2823. 4-Toluenesulfonylhydrazide

[877-66-7] **$C_7H_{10}N_2O_2S$**

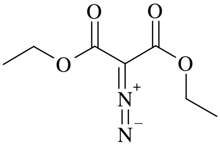


Hansell, D. P. *et al., Chem. & Ind.*, 1975, 464

While drying in a tray dryer at 60°C, a batch decomposed fairly exothermically but without fire. As a blowing agent, it is designed to have limited thermal stability [1]. One of the more recently calculated values of 87° and 78°C for induction periods of 7

and 60 days, respectively, for critical ignition temperature coincides with the previous value of 87°/7 days. Autocatalytic combustion is exhibited.
See other BLOWING AGENTS

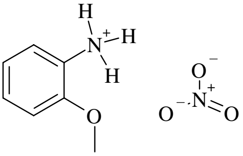
2824. Diethyl diazomalonate
[5256-74-6] **$C_7H_{10}N_2O_4$**



DOC 5, 1982, Vol. 2, 1588

It may explode during distillation at low pressure.
See other DIAZO COMPOUNDS

2825. 2-Methoxyanilinium nitrate
[ ] **$C_7H_{10}N_2O_4$**



1. Vervalin, C. H., *Hydrocarb. Process.*, 1976, **55**(9), 321
2. *See entry* HIGH RATE DECOMPOSITION

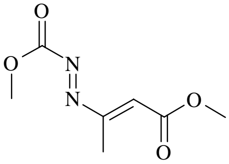
Use of a screw feeder to charge a reactor with the 2-anisidine salt led to ignition of the latter. It was known that the salt would decompose exothermically above 140°C, but later investigation showed that lower-quality material could develop an exotherm above 46°C under certain conditions [1]. Fast flame propagation occurs on moderately heating anisidine nitrate powder [2].

Sulfuric acid

Vervalin, C. H., *Hydrocarb. Process.*, 1976, **55**(9), 321

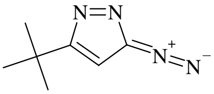
In a process for preparation of 2-methoxy-5-nitroaniline the anisidine salt was added to stirred sulfuric acid. An accidental deficiency of the latter prevented proper mixing and dissipation of the heat of solution, and local decomposition spread through the entire content of the 2000 l vessel, attaining red heat.
See other OXOSALTS OF NITROGENOUS BASES, SULFONATION INCIDENTS
See related AMINOMETHOXY COMPOUNDS

2826. Methyl 3-methoxycarbonylazocrotonate
[63160-33-8] **$C_7H_{10}N_2O_4$**



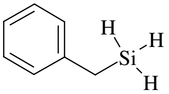
Sommer, S., *Tetrahedron Lett.*, 1977, 117
Attempted high-vacuum fractional distillation of an isomeric mixture (10% *cis*-) led to explosive decomposition. The 'diene' polymerises if stored at 20°C.
See other AZO COMPOUNDS

2827. 5-*tert*-Butyl-3-diazo-3*H*-pyrazole
[62072-11-1] **$C_7H_{10}N_4$**



The light-sensitive and piezosonic crystalline solid explodes at 97°C.
See entry DIAZOAZOLES
See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS

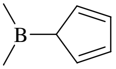
2828. Benzylsilane
[766-06-3] **$C_7H_{10}Si$**



491M, 1975, 58

It ignites in air.
See other BENZYL COMPOUNDS
See related ALKYLSILANES

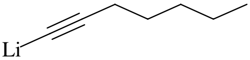
2829. Cyclopentadienyldimethylborane
[ ] **$C_7H_{11}B$**



Herberich, G. E. *et al., Organometallics,* 1996, **15**(1), 58
Spontaneously inflames in air.
See other ALKYLBORANES

2830. Lithium 1-heptynide

[42017-07-2] **$C_7H_{11}Li$**



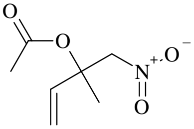
Ammonia, Iodine

See Iodine: Ammonia, Lithium 1-heptynide

See other METAL ACETYLIDES

2831. 3-Methyl-4-nitro-1-buten-3-yl acetate

[61447-07-2] **$C_7H_{11}NO_4$**



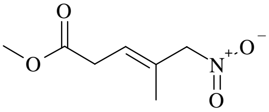
Wehrli, P. A. *et al., J. Org. Chem.*, 1977, **42**, 2940

This and the isomeric nitroester (below), both produced in the nitroacetoxylation of isoprene, are of limited thermal stability and it is recommended that neither be heated above 100°C, either neat or in solution. Vacuum distillation of the nitro esters should be limited to 1 g portions, as decomposition 'fume-offs' have been observed.

See related NITROALKENES

2832. 3-Methyl-4-nitro-2-buten-1-yl acetate

[61447-06-1] **$C_7H_{11}NO_4$**

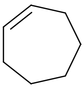


See 3-Methyl-4-nitro-1-buten-3-yl acetate

See related NITROALKENES

†2833. Cycloheptene

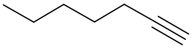
[628-92-2] **C_7H_{12}**



See related ALKENES

†2834. 1-Heptyne

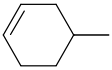
[628-71-7] **C_7H_{12}**



See other ALKYNES

†2835. 4-Methylcyclohexene

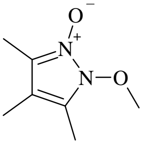
[591-47-9] **C_7H_{12}**



See related ALKENES

2836a. 1-Methoxy-3,4,5-trimethylpyrazole *N*-oxide

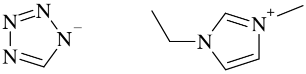
[39753-42-9] **$C_7H_{12}N_2O_2$**



Boyle, F. T. *et al., J. Chem. Soc., Perkin Trans. 1*, 1973, 167
It is thermally unstable and exploded during attempted distillation.
See 1-Methoxyimidazole *N*-oxide
See other N—O COMPOUNDS, N-OXIDES

2836b. 1-Ethyl-3-methylimidazolium tetrazolide

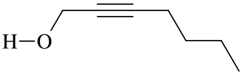
[ ] **$C_7H_{12}N_6$**



Ogihara, W. *et al., Chem. Let.*, 2004, **33**(8), 1022
An ionic liquid optimistically claimed to be useful as a solvent or an explosive.
See other TETRAZOLES

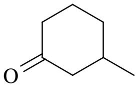
2837. 2-Heptyn-1-ol

[1002-36-4] **$C_7H_{12}O$**



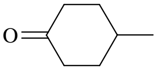
Brandsma, 1971, 69
Dilution of the alcohol with white mineral oil before vacuum distillation is recommended to avoid the possibility of explosion of the undiluted distillation residue.
See other ACETYLENIC COMPOUNDS

2838. 3-Methylcyclohexanone
[591-24-2] **$C_7H_{12}O$**



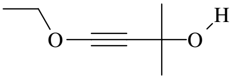
Hydrogen peroxide, Nitric acid
See Hydrogen peroxide: Ketones, etc.

2839. 4-Methylcyclohexanone
[589-92-4] **$C_7H_{12}O$**



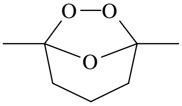
Nitric acid
See Nitric acid: 4-Methylcyclohexanone

2840. 4-Ethoxy-2-methyl-3-butyn-2-ol
[2041-76-1] **$C_7H_{12}O_2$**



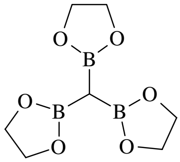
Brandsma, 1971, 78
Traces of acid adhering to glassware are sufficient to induce explosive decomposition of the alcohol during distillation, and must be neutralised by pre-treatment with ammonia gas. Low pressures and temperatures are essential during distillation. Explosions during distillation using water pump vacuum and bath temperatures above 115°C were frequent.
See ETHOXYETHYNYL ALCOHOLS
See other ACETYLENIC COMPOUNDS, CATALYTIC IMPURITY INCIDENTS

2841a. 1,2-Dimethylcyclopentene ozonide
(1,5-Dimethyl-6,7,8-trioxabicyclo[3.2.1]octane)
[19987-14-5] $C_7H_{12}O_3$



Criegee, R. *et al., Ber.*, 1953, **86**, 3
Though the ozonide appeared stable to small-scale high-vacuum distillation, the residue exploded violently at 130°C.
See other OZONIDES

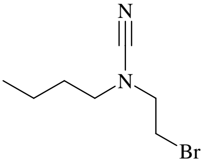
2841b. Tris(ethylenedioxyboryl)methane (Methylidynetris(1,3,2-dioxaborolane))
[83622-41-7] $C_7H_{13}B_3O_6$



Preparative hazard

Schummer, D. *et al., Tetrahedron*, 1995, **51**(41), 11219
The insoluble residue from this improved preparation (probably arising from the initial reaction between lithium, chlorodimethoxyborane and chloroform to make tris(dimethoxyboryl)methane) may be pyrophoric, even though lithium is used in deficiency.

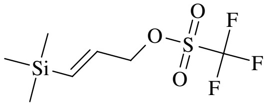
2842. *N*-Cyano-2-bromoethylbutylamine
[ ] $C_7H_{13}BrN_2$



Anon., *BCISC Quart. Safety Summ.*, 1964, **35**, 23
A small sample heated to 160°C decomposed exothermically, reaching 250°C. It had previously been distilled at 95°/0.65 mbar without decomposition.
See N-Cyano-2-bromoethylcyclohexylamine
See other CYANO COMPOUNDS

2843. 3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate

[62905-84-4] $C_7H_{13}F_3O_3SSi$

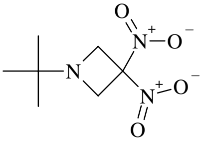


See entry ALLYL TRIFLUOROMETHANESULFONATES

See other ALLYL COMPOUNDS, SULFUR ESTERS

2844. *N*-Dimethylethyl-3,3-dinitroazetidine (*N-tert*-Butyl-3,3-dinitroazetidine)

[125735-38-8] $C_7H_{13}N_3O_4$



Archibald, T. G. *et al., J. Org. Chem.*, 1990, **55**, 2920

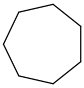
The above compound, prepared as an intermediate to 1,3,3-trinitroazetidine for study as an explosive, decomposed explosively when heated above 120°C for distillation. Precautions when handling nitroazetidines are counselled.

See other STRAINED-RING COMPOUNDS

See related POLYNITROALKYL COMPOUNDS

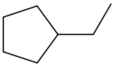
†2845. Cycloheptane

[291-64-5] C_7H_{14}



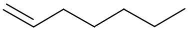
†2846. Ethylcyclopentane

[1640-89-7] C_7H_{14}



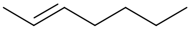
†2847. 1-Heptene

[592-76-7] C_7H_{14}



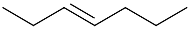
See other ALKENES

†2848. 2-Heptene
[592-77-8] **C_7H_{14}**



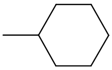
See other ALKENES

†2849. 3-Heptene
[592-78-9] **C_7H_{14}**



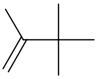
See other ALKENES

†2850. Methylcyclohexane
[108-87-2] **C_7H_{14}**



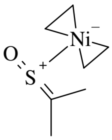
HCS 1980, 646

†2851. 2,3,3-Trimethylbutene
[594-56-9] **C_7H_{14}**



See other ALKENES

2852. Dimethylmethyleneoxosulfanenickel(0) diethylene complex
[ ] **$C_7H_{14}NiOS$**

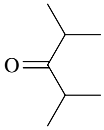


Pörschke, K. R., *Chem. Ber.*, 1987, **120**, 425—427

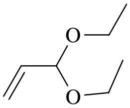
The complex decomposes violently at 0°C, evolving ethane, cyclopropane and methane.

See other GAS EVOLUTION INCIDENTS, HEAVY METAL DERIVATIVES

†2853. 2,4-Dimethyl-3-pentanone
[565-80-0] **$C_7H_{14}O$**

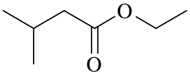


†2854. 3,3-Diethoxypropene
[3054-95-3] **$C_7H_{14}O_2$**

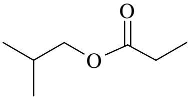


See other PEROXIDISABLE COMPOUNDS

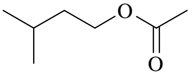
†2855. Ethyl isovalerate
[108-64-5] **$C_7H_{14}O_2$**



†2856. Isobutyl propionate
[540-42-1] **$C_7H_{14}O_2$**

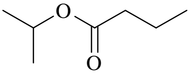


†2857. Isopentyl acetate
[123-92-2] **$C_7H_{14}O_2$**

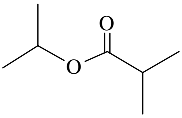


NSC 208, 1977; *FPA H117*, 1982; *HSC 1980*, 563

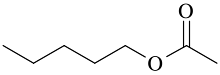
†2858. Isopropyl butyrate
[638-11-9] **$C_7H_{14}O_2$**



†2859. Isopropyl isobutyrate
[617-50-5] **$C_7H_{14}O_2$**

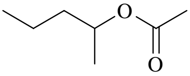


†2860. Pentyl acetate
[628-63-7] **$C_7H_{14}O_2$**



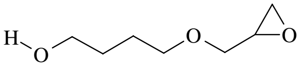
HCS 1980, 153

†2861. 2-Pentyl acetate
[53496-15-4] **$C_7H_{14}O_2$**



HCS 1980, 154

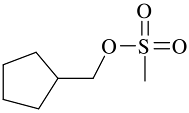
2862a. 4(2,3-Epoxypropoxy)butanol
[4711-95-9] **$C_7H_{14}O_3$**



Trichloroethylene
See Trichloroethylene: Epoxides
See other 1,2-EPOXIDES

2862b. Cyclopentylmethyl methanesulfonate

[73017-76-2] **$C_7H_{14}O_3S$**



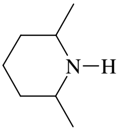
It decomposes vigorously at 128°C.

See entry SULFONIC ACID ESTERS

See other SULFUR ESTERS

†2863. 2,6-Dimethylpiperidine

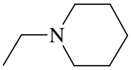
[504-03-0] **$C_7H_{15}N$**



See other ORGANIC BASES

†2864. 1-Ethylpiperidine

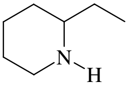
[766-09-6] **$C_7H_{15}N$**



See other ORGANIC BASES

†2865. 2-Ethylpiperidine

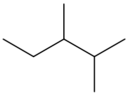
[1484-80-6] **$C_7H_{15}N$**



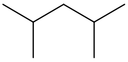
See other ORGANIC BASES

†2866. 2,3-Dimethylpentane

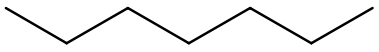
[565-59-3] **C_7H_{16}**



†2867. 2,4-Dimethylpentane
[108-08-7] **C_7H_{16}**

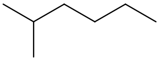


†2868. Heptane
[142-82-5] **C_7H_{16}**

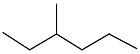


HCS 1980, 524 (includes isomers)

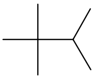
†2869. 2-Methylhexane
[591-76-4] **C_7H_{16}**



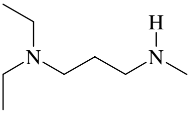
†2870. 3-Methylhexane
[589-34-4] **C_7H_{16}**



†2871. 2,2,3-Trimethylbutane
[464-06-2] **C_7H_{16}**



2872a. 3-Diethylaminopropylamine
[14642-66-1] **$C_7H_{18}N_2$**



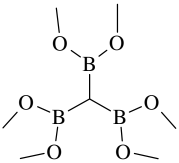
Cellulose nitrate

See CELLULOSE NITRATE: Amines

See other ORGANIC BASES

2872b. Tris(dimethoxyboryl)methane (Hexamethyl 2,2′,2″-methylidynetrisboronate)

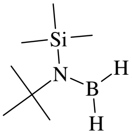
[18067-51-1] **$C_7H_{19}B_3O_6$**



See Tris(ethylenedioxyboryl)methane

2873a. *N-tert*-Butyl-*N*-trimethylsilylaminoborane

[73452-32-1] **$C_7H_{20}BNSi$**



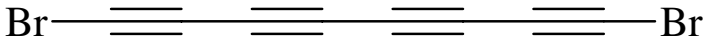
Wisian-Nielsen, P. *et al., J. Inorg. Nucl. Chem.*, 1979, **41**, 1546

It ignites in direct contact with air.

See related ALKYLSILANES, BORANES

2873b. Dibromooctatetrayne

[259235-75-1] **C_8Br_2**



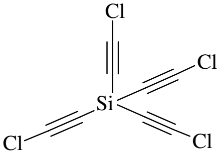
Dembinski, R. *et al., J. Amer. Chem. Soc.*, 2000, **122**(5), 810

Like lower homologues, this is explosive. Violent detonations made it unusable as a synthetic reagent.

See other HALOACETYLENE DERIVATIVES

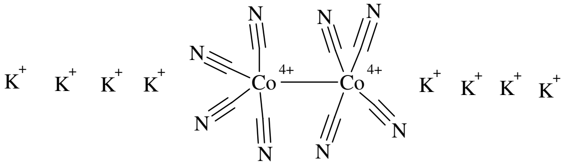
2874. Tetrakis(chloroethynyl)silane

[ ] **C_8Cl_4Si**



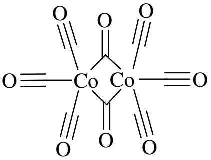
Viehe, H. G., *Chem. Ber.*, 1959, **92**, 3075
Though thermally stable, it exploded violently on grinding (with potassium bromide) or on impact.
See other FRICTIONAL INITIATION INCIDENTS, HALOACETYLENE DERIVATIVES

2875. Potassium octacyanodicobaltate(8—)
[23705-25-1] **$C_8Co_2K_8N_8$**



Bailar, 1973, Vol. 4, 175
A very unstable, pyrophoric material.
See other METAL CYANIDES (AND CYANO COMPLEXES), PYROPHORIC MATERIALS

2876. Octacarbonyldicobalt
[10210-68-1] **$C_8Co_2O_8$**



Wender, I. *et al., Inorg. Synth.*, 1957, **5**, 191
When the carbonyl is prepared (by rapid cooling) as a fine powder, it decomposes in air to give pyrophoric dodecacarbonyltetracobalt.
See other CARBONYLMETALS

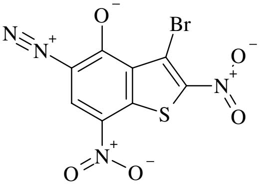
2877. Caesium graphite
[12079-66-2] **C_8Cs**

CsC_8

See Carbon: Alkali metals
See other METAL NON-METALLIDES

2878a. 3-Bromo-2,7-dinitrobenzo[*b*]thiophene-5-diazonium-4-oxide

[ ] **$C_8HBrN_4O_5S$**



Brown, I. *et al., Chem. & Ind.*, 1962, 982

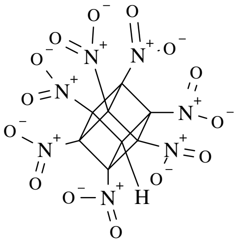
It is an explosive compound.

See Nitric acid: Benzo[*b*]thiophene derivatives

See other ARENEDIAZONIUM OXIDES

2878b. Heptanitrocubane

[99393-62-1] **$C_8HN_7O_{14}$**



1. Eaton, P. *et al., Angewand. (Int.)*, 2000, **39**, 401
2. Editor's comment

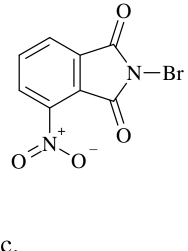
The compound is highly acidic (as well as highly explosive) and deflagrates on contact with traces of pyridine [1]. An *aci*-intermediate would appear improbable [2].

See also aci-NITROQUINONOID COMPOUNDS, NITROALKANES

See other CUBANES

2879. *N*-Bromo-3-nitrophthalimide

[ ] **$C_8H_3BrN_2O_4$**



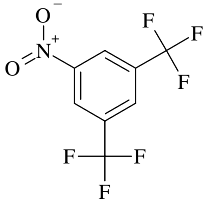
Tetrahydrofurfuryl alcohol

See N-HALOIMIDES: Alcohols etc.

See other N-HALOGEN COMPOUNDS, NITROARYL COMPOUNDS

2880. 1,3-Bis(trifluoromethyl)-5-nitrobenzene

[328-75-6] **$C_8H_3F_6NO_2$**



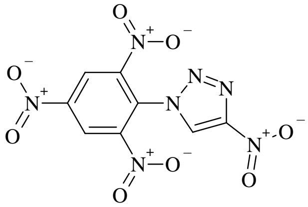
Preparative hazard

See Nitric acid: 1,3-Bis(trifluoromethyl)benzene

See other NITROARYL COMPOUNDS

2881. 4-Nitro-1-picryl-1,2,3-triazole

[31123-28-1] **$C_8H_3N_7O_8$**



Storm, C. B. *et al., J. Phys. Chem.*, 1989, **93**, 1000—1007

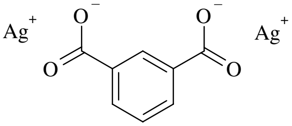
Though the 1- and 2-picryl isomers are similarly explosive, the former has a much higher impact-sensitivity than the latter. This is attributed to the former having a shorter N2 to N3 interatomic distance, longer adjacent bonds, and a lower activation energy for elimination of molecular nitrogen from the 2,3 positions.

See 5-nitro-2-picryltetrazole, 1-Picryl-1,2,3-triazole

See other POLYNITROARYL COMPOUNDS, TRIAZOLES

2882a. Silver isophthalate

[57664-97-8] **$C_8H_4Ag_2O_4$**



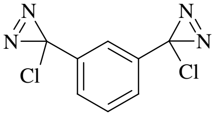
Fields, E. K., *J. Org. Chem.*, 1976, **41**, 918—919

Decomposition of the salt at 375°C under nitrogen, with subsequent cooling under hydrogen, gives a black carbon-like polymer containing metallic silver which ignites at 25°C on exposure to air.

See other SILVER COMPOUNDS

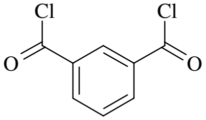
See related PYROPHORIC MATERIALS

2882b. 1,3-Phenylenebis(chlorodiazirine)
[155305-75-2] **$C_8H_4Cl_2N_4$**



Bonneau, R. *et al., J. Photochem. & Photobiol.*, 2003, **161**(1), 43
Explosive, it may be handled safely in solution but should be stripped only in small quantities and the product never allowed to freeze.
See other DIAZIRINES

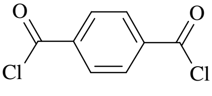
2883. Isophthaloyl chloride
[99-63-8] **$C_8H_4Cl_2O_2$**



Methanol
Morrell, S. H., private comm., 1968
Violent reaction occurred between isophthaloyl chloride and methanol when they were accidentally added in succession to the same waste solvent bottle.
See other ACYL HALIDES

Preparative hazard
See 1,3-Bis(trichloromethyl)benzene: Oxidants

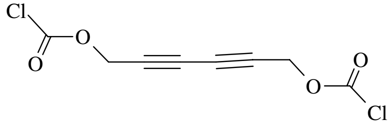
2884. Terephthaloyl chloride (1,4-Benzenedicarbonyl chloride)
[100-20-9] **$C_8H_4Cl_2O_2$**



Water
Anon., *Loss Prev. Bull.*, 1986, (071), 9
Hydrolysis of 7 t of the acid chloride by water in a herbicide processing unit ran out of control, gas evolution eventually rupturing the reactor violently.
See other ACYL HALIDES, GAS EVOLUTION INCIDENTS

2885. 2,4-Hexadiynylene chloroformate

[ ] **$C_8H_4Cl_2O_4$**



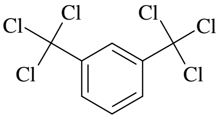
Driedger, P. E. *et al., Chem. Eng. News*, 1972, **50**(12), 51

One sample exploded with extreme violence at 15°C/0.2 mbar, while another smaller sample had been distilled uneventfully at 114—115°C/0.2 mbar.

See other ACETYLENIC COMPOUNDS, ACYL HALIDES

2886. 1,3-Bis(trichloromethyl)benzene

[881-99-2] **$C_8H_4Cl_6$**



Oxidants

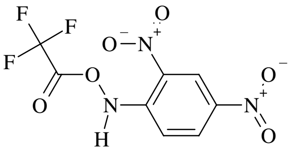
Rondevstedt, C. S., *J. Org. Chem.*, 1976, **41**, 3574—3577

Heating the bis(trichloromethyl)benzene with potassium nitrate, selenium dioxide or sodium chlorate to effect conversion to the bis(acyl chloride) led to eruptions at higher temperatures, and was too dangerous to pursue.

See related HALOALKANES, HALOARYL COMPOUNDS

2887. *N*-Trifluoroacetoxy-2,4-dinitroaniline

[127526-90-3] **$C_8H_4F_3N_3O_6$**



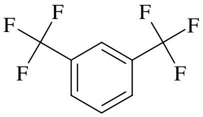
Bryant, I. R. *et al., Austr. J. Chem.*, 1989, **42**(12), 2275

The crude compound was isolated, began to evolve trifluoroacetic acid and, after 15 minutes, exploded.

See other N—O COMPOUNDS

2889. 1,3-Bis(trifluoromethyl)benzene

[402-31-3] **$C_8H_4F_6$**



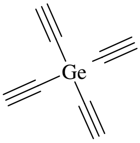
Nitric acid, Sulfuric acid

See Nitric acid: 1,3-Bis(trifluoromethyl)benzene, etc.

See related HALOALKANES, HALOARYL COMPOUNDS

2890. Tetraethynylgermanium

[4531-35-5] **C_8H_4Ge**



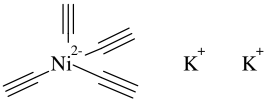
1. Chokiewicz, W. *et al., Compt. rend.*, 1960, **250**, 866
2. Shikkiev, I. A. *et al., Doklad. Akad. Nauk SSSR*, 1961, **139**, 1138 (Engl. transl., 830)

It explodes on rapid heating [1], or friction [2].

See other METAL ACETYLIDES

2891. Potassium tetraethynylnickelate(2—)

[65664-23-5] **$C_8H_4K_2Ni$**



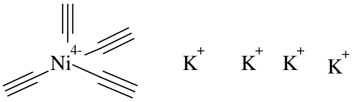
Air, or Water

Vigorously pyrophoric in air, it may explode on contact with drops of water.

See entry COMPLEX ACETYLIDES

2892. Potassium tetraethynylnickelate(4—)

[ ] **$C_8H_4K_4Ni$**

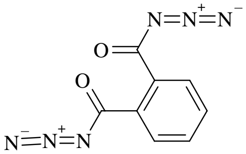


The diammoniate (and that of the sodium salt) explodes on exposure to impact, friction or flame.

See entry COMPLEX ACETYLIDES

2893a. Phthaloyl diazide

[50906-29-1] **$C_8H_4N_6O_2$**



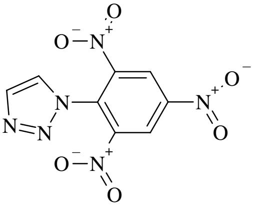
Lindemann, H. *et al., Ann.*, 1928, **464**, 237

The *symm*-diazide is extremely explosive, while the *asymm*-isomer (X) is less so, melting at 56°C, but exploding on rapid heating.

See other ACYL AZIDES

2893b. 1-Picryl-1,2,3-triazole

[18922-71-9] **$C_8H_4N_6O_6$**



Storm, C. B. *et al., J. Phys. Chem.*, 1989, **93**, 1000—1007

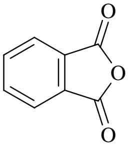
Though the 1- and 2-picryl isomers are similarly explosive, the former has a much higher impact-sensitivity than the latter. This is attributed to the former having a shorter N2 to N3 interatomic distance, longer adjacent bonds, and a lower activation energy for elimination of molecular nitrogen from the 2,3 positions.

See 4-Nitro-1-picryl-1,2,3-triazole

See other POLYNITROARYL COMPOUNDS, TRIAZOLES

2894. Phthalic anhydride

[85-44-9] **$C_8H_4O_3$**



HCS 1980, 752

Other reactants

Yoshida, 1980, 357

MRH Values calculated for 11 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Copper(II) oxide: Phthalic acid, etc.	MRH 2.09/tr.
Nitric acid: Phthalic anhydride	MRH 5.52/71
Sodium nitrite: Phthalic acid, etc.	MRH 2.09/tr.

See other ACID ANHYDRIDES

Preparative hazard

1. Kratochvil, V., *Chem. Abs.*, 1974, **80**, 3215
2. English transl. by D. S. Rosenberg, 10.2.69 of German transl. by S. Vedrilla (Chemiebau) of 'Low Temperature Pyrophoric Compounds in Process for Preparing Phthalic Anhydride', a Japanese paper in *Anzen Kogyo Kogaku*, 1968
3. Schwab, R. F. *et al., Chem. Eng. Progr.*, 1970, **66**(9), 49—53

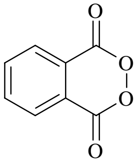
Investigation of an explosion in a phthalic anhydride plant showed that naphthoquinones (by-products from naphthalene oxidation) reacted with iron(III) salts of phthalic, maleic or other acids (corrosion products) to form labile materials. The latter were found to undergo exothermic oxidation and self-ignition at around 200°C. Process conditions to minimise hazards are discussed, with 27 references [1]. Fires and explosions in the condenser sections of phthalic anhydride plants were traced to the presence of deposits of thermally unstable basic iron salts of maleic or phthalic acids and iron sulfides derived from sulfur in the naphthalene feedstock. A small-scale laboratory test procedure was developed to measure the exotherm point and maximum temperature rise in various mixtures of materials found to be present in the condensing section. A basic iron(III) maleate hydrate showed an exotherm point of 165°C and temperature rise of 369°C, changed by pre-treatment with hydrogen sulfide to 164 and 392°C, respectively. The corresponding figures for basic iron(III) phthalate were 236 and 477°C, both unchanged by pre-sulfiding treatment. The part played by acid-corrosion of the mild steel condensers in formation of the unstable pyrophoric compounds was also investigated. It was concluded that the origins of the many mishaps which have occurred soon after plant start-up were explicable in terms of these experimental findings [2]. Other hazards in phthalic anhydride production units have also been discussed [3].

See PYROPHORIC IRON—SULFUR COMPOUNDS

See other CORROSION INCIDENTS

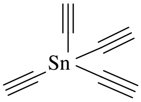
2895. Phthaloyl peroxide (2,3-Benzodioxin-1,4-dione)

[4733-52-2] **$C_8H_4O_4$**



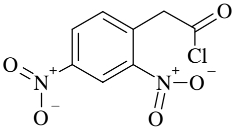
Jones, M. *et al., J. Org. Chem.*, 1971, **36**, 1536
Detonable by impact or by melting at 123°C. It may be a linear polymer, rather than the cyclic structure implied by the alternative name.
See other DIACYL PEROXIDES

2896. Tetraethynyltin
[16413-88-0] **C_8H_4Sn**



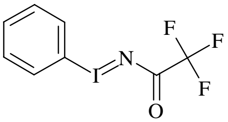
Jenkner, H., Ger. Pat. 115 736, 1961
It explodes on rapid heating.
See other METAL ACETYLIDES

2897. 2,4-Dinitrophenylacetyl chloride
[109799-62-4] **$C_8H_5ClN_2O_5$**



Bonner, T. G., *J. R. Inst. Chem.*, 1957, **81**, 596
Explosive decomposition occurred during attempted vacuum distillation, attributed either to the presence of some trinitro compound in the unpurified dinitrophenylacetic acid used, or to the known instability of *o*-nitro acid chlorides. A previous publication (ibid., 407) erroneously described the decomposition of 2,4-dinitrobenzoyl chloride.
See other NITROACYL HALIDES

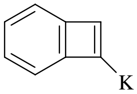
2898. Trifluoroacetyliminoiodobenzene
[94286-09-6] **$C_8H_5F_3INO$**



Mansuy, D. *et al., J. Chem. Soc., Chem. Comm.*, 1984, 1163
The solid undergoes explosive decomposition at 100°C.
See other N-HALOGEN COMPOUNDS, IODINE COMPOUNDS

2899. 3-Benzocyclobutenylpotassium

[ ] **C_8H_5K**



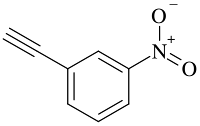
Perchloryl fluoride

See Perchloryl fluoride: Benzocyclobutene, etc.

See related ARYLMETALS

2900. 3-Nitrophenylacetylene

[3034-94-4] **$C_8H_5NO_6$**



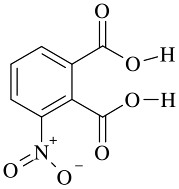
Sorbe, 1968, 152

The compound (isomer not stated) and its metal derivatives are explosive.

See other ALKYNES, NITROARYL COMPOUNDS

2901a. 3-Nitrophthalic acid

[603-11-2] **$C_8H_5NO_6$**



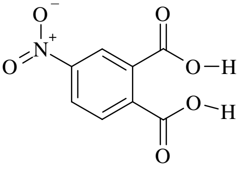
Preparative hazard

See Nitric acid: Phthalic anhydride, etc.

See other NITROARYL COMPOUNDS, ORGANIC ACIDS

2901b. 4-Nitrophthalic acid

[610-27-5] **$C_8H_5NO_6$**

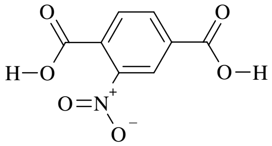


Lanthanide salts are reported as decomposing explosively on heating.

See LANTHANIDE NITROBENZOATES

2902. Nitroterephthalic acid

[603-11-2] **$C_8H_5NO_6$**



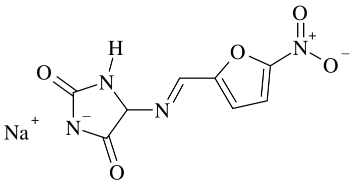
Preparative hazard

See Nitric acid: Sulfuric acid, Terephthalic acid

See other NITROARYL COMPOUNDS, ORGANIC ACIDS

2903. 3-Sodio-5-(5’-nitro-2’-furfurylideneamino)imidazolidin-2,4-dione

[54-87-5] **$C_8H_5N_4NaO_5$**



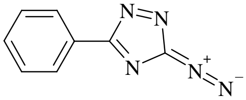
Boros, L. et al., Ger. Offen., 2 328 927, 1974

The crystalline *N*-sodium salt is explosive.

See other N-METAL DERIVATIVES

2904. 3-Diazo-5-phenyl-3*H*-1,2,4-triazole

[80670-36-6] **$C_8H_5N_5$**



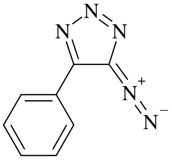
It is a light-sensitive and highly shock-sensitive solid, which can be weighed or stored in the dark at ambient temperature as the dry solid, but it decomposes in solution in a few hours.

See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

2905. 4-Diazo-5-phenyl-1,2,3-triazole

[64781-77-7] **$C_8H_5N_5$**



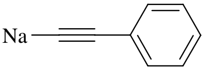
The crystalline solid explodes at the m.p., 133—5°C

See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

2906. Sodium phenylacetylide

[1004-22-4] **C_8H_5Na**



Nef, J. U., *Ann.*, 1899, **308**, 264

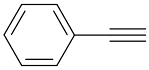
The ether-moist powder ignites in air.

See ALKALI-METAL DERIVATIVES OF HYDROCARBONS

See other METAL ACETYLIDES

2907. Phenylacetylene

[536-74-3] **C_8H_6**



Palladium(II) acetate

Trumbo, D. L. *et al., J. Polym. Sci., A, Polymer Chem.*, 1987, **25**, 1027—1034

Among palladium(II) salts used to polymerise phenylacetylene, the acetate led to rapid and very exothermic polymerisation, sometimes leading to explosion.

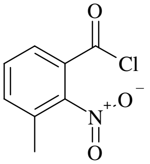
See other POLYMERISATION INCIDENTS

Perchloric acid

See Perchloric acid: Phenylacetylene

See other ALKYNES

2908. 3-Methyl-2-nitrobenzoyl chloride
[50424-93-6] **$C_8H_6ClNO_3$**

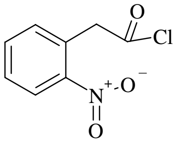


1. Dahlbom, R., *Acta Chem. Scand.*, 1960, **14**, 2049
2. Anon., *Loss Prev. Bull.*, 1977, (013), 16

Attempted distillation caused an explosion [1], and a 200 g sample deflagrated at 120—130°C under high vacuum [2].

See other NITROACYL HALIDES

2909. 2-Nitrophenylacetyl chloride
[22751-23-1] **$C_8H_6ClNO_3$**

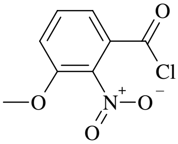


Hayao, S., *Chem. Eng. News*, 1964, **42**(13), 39

Distillation of solvent chloroform from the preparation caused the residue to explode violently on 2 occasions. Previous publications had recommended use of solutions of the chloride, in preference to isolated material.

See other NITROACYL HALIDES

2910. 3-Methoxy-2-nitrobenzoyl chloride
[15865-57-3] **$C_8H_6ClNO_4$**



1. Goodwin, B., *Chem. Brit.*, 1987, **23**, 1180—1181
2. Bretherick, L., *Chem. Brit.*, 1988, **24**, 125

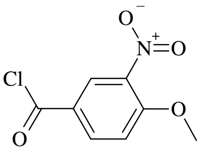
During an attempt to prepare 3-methoxy-2-nitrobenzoyl cyanide by heating the title chloride with copper(I) cyanide to over 200°C, the reaction mixture had decomposed vigorously at around 60°C. This was attributed to thermal instability of the intended product [1], but available evidence suggests that instability of the title nitroacyl halide is a much more likely cause. However, there is also the possibility of a reaction involving demethylation of the methoxynitrobenzoyl chloride by traces of hydrogen chloride, and of a subsequent polycondensation reaction of the hydroxynitroacyl chloride so formed and of its subsequent exothermic decomposition, analogous to that of the 4-methoxy-3-nitro isomer. The presence of the copper salt would be expected to catalyse either of the possibilities of exothermic reaction [2].

See 4-Methoxy-3-nitrobenzoyl chloride

See entry NITROACYL HALIDES

2911. 4-Methoxy-3-nitrobenzoyl chloride

[10397-28-1] **$C_8H_6ClNO_4$**



Preparative hazard

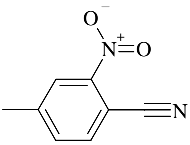
Grewer, T. *et al., Chem. Ing. Tech.*, 1977, **49**, 562—563

Preparation of the acid chloride by an established procedure involved heating the acid with sulfinyl chloride, finally at 100°C for 4 h, when evolution of hydrogen chloride and sulfur dioxide was complete (and the vessel appears then to have been isolated from the gas absorption system). An apparently normally completed batch led to a double explosion with rupture of the process vessel. Subsequent thermoanalytical investigation revealed that the nitroacyl chloride is demethylated by hydrogen chloride produced in the primary reaction, methyl chloride being formed as well as the hydroxyacyl chloride. The latter condenses to form a poly(nitrophenylcarboxylic ester) and hydrogen chloride, which can lead to further demethylation. The sequence of exothermic reactions leads to accelerating decomposition, which becomes violent at about 350—380°C, with generation of pressure up to 40 bar by the volatiles produced. The double explosion was attributed to ignition of chloromethane, followed by that of the decomposing poly(nitro ester). Preventive measures are discussed.

See other GAS EVOLUTION INCIDENTS, NITROACYL HALIDES, POLYCONDENSATION REACTION INCIDENTS

2912. 4-Cyano-3-nitrotoluene

[26830-95-5] **$C_8H_6N_2O_2$**



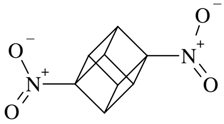
Preparative hazard

See 4-Chloro-3-nitrotoluene: Copper(I) cyanide, Pyridine

See other CYANO COMPOUNDS, NITROARYL COMPOUNDS

2913. 1,4-Dinitropentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane

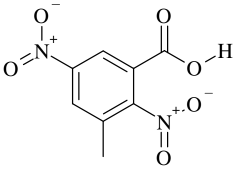
[87830-30-6] **$C_8H_6N_2O_4$**



See entry CUBANES

2914. 2,5-Dinitro-3-methylbenzoic acid

[70343-15-6] **$C_8H_6N_2O_6$**



Oleum, Sodium azide

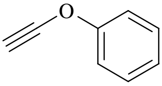
Nielsen, A. T. *et al., J. Org. Chem.*, 1979, **44**, 2504

Addition of sodium azide to a solution of the acid in 20% oleum at 5—10°C to produce 3-amino-2,5-dinitrotoluene must be slow (0.1 g portions during 1 h) to avoid explosion.

See other ORGANIC ACIDS, POLYNITROARYL COMPOUNDS

2915. Phenoxyacetylene

[4279-76-9] **C_8H_6O**



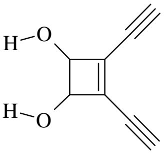
Jacobs, T. L. *et al., J. Amer. Chem. Soc.*, 1942, **64**, 223

Small samples heated rapidly in sealed tubes to around 100°C exploded.

See other ACETYLENIC COMPOUNDS

2916. *cis*-3,4-Diethynylcyclobut-3-ene-1,2-diol

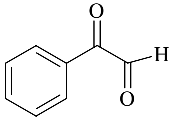
[125358-28-3] **$C_8H_6O_2$**



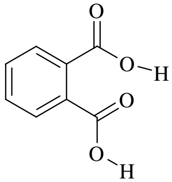
Diederich, F., *et al., J. Amer. Chem. Soc.*, 1990, **112**, 1616

The title compound explodes on heating to 55°C. The ethylene ketal of the corresponding diketone explodes at 118°C.
See 11,12-Diethynyl-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene
See other ACETYLENIC COMPOUNDS

†2917. Phenylglyoxal
[1074-12-0] **$C_8H_6O_2$**



2918. Phthalic acid
[88-99-3] **$C_8H_6O_4$**

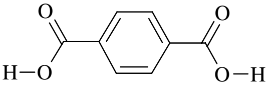


HCS 1980, 753

Other reactants
Yoshida, 1980, 298
MRH values calculated for 12 combinations with oxidants are given.

Sodium nitrite MRH 3.64/79
See Sodium nitrite: Phthalic acid
See other ORGANIC ACIDS

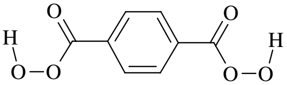
2919. Terephthalic acid
[100-21-0] **$C_8H_6O_4$**



Preparative hazard
See Nitric acid: Hydrocarbons (reference 6)
See other ORGANIC ACIDS

2920. Diperoxyterephthalic acid

[1711-42-8] **$C_8H_6O_6$**



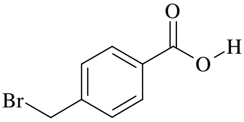
Baeyer, A. *et al., Ber.*, 1901, **34**, 762

It explodes when heated or struck.

See other PEROXYACIDS

2921. 4-Bromomethylbenzoic acid

[6232-88-8] **$C_8H_7BrO_2$**



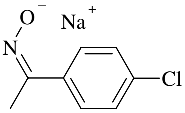
Preparative hazard

See N-Bromosuccinimide: Dibenzoyl peroxide, etc.

See other BENZYL COMPOUNDS, ORGANIC ACIDS

2922. Sodium 4-chloroacetophenone oximate

[1956-39-4] (oxime) **$C_8H_7ClNNaO$**



van Dijk, J. *et al., J. Med. Chem.*, 1977, **20**, 1201, 1205

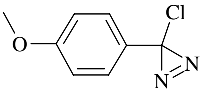
Admission of air to the evacuated container of the dry oximate led to explosion on 2 occasions: nitrogen purging is advised.

See other N—O COMPOUNDS

See related OXIMES

2923. Chloro-(4-methoxyphenyl)diazirine

[4222-26-8] **$C_8H_7ClN_2O$**

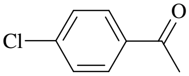


Griller, D. *et al., J. Amer. Chem. Soc.*, 1982, **104**, 5549

A cold sample decomposed violently on rapid warming to ambient temperature.

See other DIAZIRINES

2924. 4-Chloroacetophenone
[99-91-2] **C_8H_7ClO**



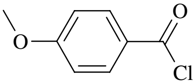
Dimethylamine

Lundstedt, T. *et al., Acta Chem. Scand., Ser. B*, 1984, **B38**, 717—719

During optimisation of a preparative procedure, heating mixtures of 4-chloroacetophenone and dimethylamine (4.22 : 1) at 234°C led to two explosions. Use of a safety screen is advised.

See other AMINATION INCIDENTS

2925. 4-Methoxybenzoyl chloride (Anisoyl chloride)
[100-07-2] **$C_8H_7ClO_2$**

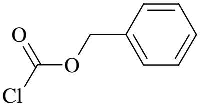


1. Carroll, D. W., *Chem. Eng. News*, 1960, **38**(34), 40
2. Ager, J. H. *et al., Chem. Eng. News*, 1960, **38**(43), 5

Two incidents involving explosion of bottles of chloride stored at ambient temperature are described [1,2]. Safe preparation with storage at 5°C is detailed [2].

See other ACYL HALIDES

2926a. Benzyl chloroformate
[501-53-1] **$C_8H_7ClO_2$**



1. Aldrich Handbook of Fine Chemicals, 2000/01
2. Lancaster Synthesis Catalogue, 2000/01

A supplier warns that it may decompose vigorously from 100°C up [1]. Another advises caution when opening bottles, since, like other chloroformates, it may pressurise on standing [2]. Decomposition will generate benzyl chloride, itself unstable

See other BENZYL COMPOUNDS

Iron salts

Anon., *Loss Prev. Bull.*, 1975, (003), 2

The ester is made by adding benzyl alcohol slowly to a preformed solution of phosgene in toluene at 12—16°C, toluene solvent finally being distilled off under vacuum. When discoloured phosgene was used (probably containing iron salts from corrosion of the cylinder), a violent explosion occurred during the distillation phase, presumably involving iron-catalysed decomposition of the chloroformate ester.

See other CATALYTIC IMPURITY INCIDENTS, CORROSION INCIDENTS

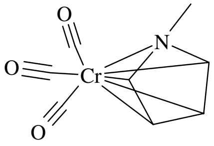
Water

See ARYL CHLOROFORMATES: Water

See related ACYL HALIDES

2926b. Tricarbonyl(1-methylpyrrole)chromium(0) (Tricarbonyl [(1,2,3,4,5-η)-1-methyl-1*H*-pyrrole]chromium)

[33506-43-3] **$C_8H_7CrNO_3$**



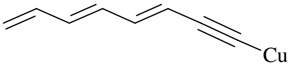
Goti, A. *et al., J. Organomet. Chem.*, 1994, **470**(1-2), C4

This half-sandwich compound is extremely pyrophoric.

See other ORGANOMETALLICS

2927. Copper 1,3,5-octatrien-7-ynide

[ ] **C_8H_7Cu**



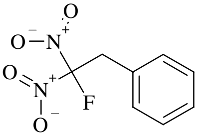
Georgieff, K. K. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 5495

It deflagrates on heating in air.

See other METAL ACETYLIDES

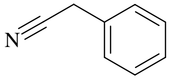
2928. 1-Fluoro-1,1-dinitro-2-phenylethane

[22692-30-4] **$C_8H_7FN_2O_4$**



See entry FLUORODINITROMETHYL COMPOUNDS (reference 4)

2929. Phenylacetonitrile
[140-29-4] **C_8H_7N**



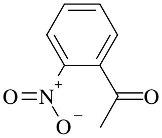
HCS 1980, 203

Sodium hypochlorite

See Sodium hypochlorite: Phenylacetonitrile

See other BENZYL COMPOUNDS, CYANO COMPOUNDS

2930. 2-Nitroacetophenone
[614-21-1] **$C_8H_7NO_3$**



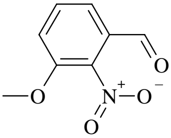
Potassium methylselenide

Leitem, L. *et al., Compt. rend. C*, 1974, **278**, 276

Interaction in dimethylformamide was explosive.

See other NITROARYL COMPOUNDS

2932. 3-Methoxy-2-nitrobenzaldehyde
[53055-05-3] **$C_8H_7NO_4$**

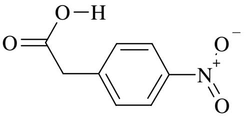


Initial decomposition temperature by DSC was 245°C.

See entry NITROBENZALDEHYDES

See other ALDEHYDES, NITROARYL COMPOUNDS

2933a. 4-Nitrophenylacetic acid
[104-03-0] **$C_8H_7NO_4$**



Acetic anhydride, Pyridine

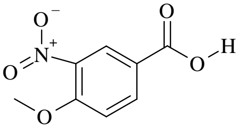
1. Batchelor, J. F., 1992, Personal communication
2. Smith, J., *J. Amer. Chem. Soc.*, 1953, **75**, 1134

The distillation residue from 0.8 molar preparation of 2-acetoxy-1(4-nitrophenyl)-prop-1-ene from reaction of the above followed by distillation, according to [2], erupted on being left to cool, spraying a fume cupboard with tar. The preparation had previously been uneventful at smaller scale [1]. The reaction is not high yielding, indicating much residue and a pot temperature perhaps in excess of 200°C to distil the product.

See other NITROARYL COMPOUNDS

2933b. 4-Methoxy-3-nitrobenzoic acid

[89-41-8] **$C_8H_7NO_5$**

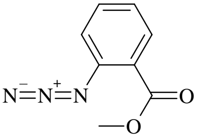


Lanthanide salts are reported as decomposing explosively on heating.

See LANTHANIDE NITROBENZOATES

2934. Methyl 2-azidobenzoate

[16714-23-1] **$C_8H_7N_3O_2$**



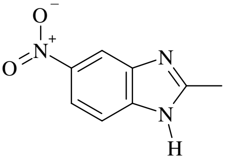
491M, 1975, 257

It exploded during distillation.

See other ORGANIC AZIDES

2935. 2-Methyl-5-nitrobenzimidazole

[1792-40-1] **$C_8H_7N_3O_2$**



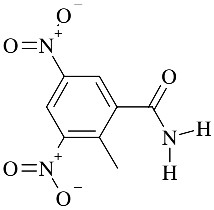
Safe preparation

See Nitric acid: 2-Methylbenzimidazole, etc.

See other NITROARYL COMPOUNDS

2936a. 3,5-Dinitro-2-toluamide

[148-01-6] **$C_8H_7N_3O_5$**



1. *The Explosion at the Dow Chemical Factory, King's Lynn 27th June 1976*, London, Health & Safety Executive, HMSO, 1977
2. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74

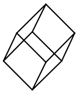
A 1.3 t batch of off-spec. material had been redried in a rotating double cone vacuum drier heated by steam to around 120—130°C for 23 h. It was left in the drier after heating had been discontinued (though cooling was not applied) and air had been allowed in, to await discharge the next working day. After 2 h, a violent explosion occurred causing one fatality and much destruction. Later investigation of the stability of the compound, notably by ARC techniques, showed that the excessively long drying time had probably caused the onset of thermal decomposition while heat was still being applied, and that further storage under virtually adiabatic conditions would have led to the steady acceleration of the exothermic decomposition to the point of explosion. At this point, it was estimated that a temperature in excess of 800°C had been attained in the drier at detonation, when the shock wave would generate a pressure approaching 800 bar. DSC techniques had shown exotherms at 273° for unheated material, and of 248—259 for material which had been preheated using conditions thought to be present in the drier [1]. The finely powdered amide is also a significant dust explosion hazard, maximum explosion pressures of 10.4 bar and a maximum rate of rise above 680 bar/s having been determined [2].

See DRYING, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

See other POLYNITROARYL COMPOUNDS

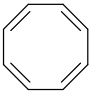
2936b. Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane

[277-10-1] **C_8H_8**



See entry CUBANES

†2937. 1,3,5,7-Cyclooctatetraene
[629-20-9] **C_8H_8**



The tetraene is endothermic by some 2.5 kJ/g; which is about the energy of explosion of old-fashioned black powder.

Dimethyl acetylenedicarboxylate

1. Bianchi, G., *Chem. in Brit.*, 1996, **32**(8), 22

In an attempt to obtain a 1:1 Diels Alder adduct, small quantities were sealed into a steel bomb and incubated in an oven at 140°C. After a time there was a violent explosion, converting the oven to an irregular perforated sphere [1]. The editor suspects that the bursting bomb released flammable vapours that ignited in the cubic oven, distorting the shapnel punctured body.

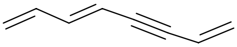
See Lithium perchlorate: Diethyl ether

Oxygen

See Oxygen: Cyclooctatetraene

See related DIENES

2938. 1,3,7-Octatrien-5-yne
[16607-77-5] **C_8H_8**

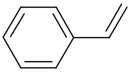


1. Nieuwland, J. A. *et al., J. Amer. Chem. Soc.*, 1931, **53**, 4201
2. Dolgopolski, I. M. *et al., Chem. Abs.*, 1948, **42**, 4517e
3. Georgieff, K. K. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 5495

This tetramer of acetylene decomposes violently on distillation at 156°C, but not at reduced pressure [1]. It polymerises on standing to a solid detonable by shock [2]. Explosions occurred during attempted analytical combustion [3].

See related ALKYNES, DIENES

2940. Styrene (Ethenylbenzene)
[100-42-5] **C_8H_8**



(*MCA SD-37*, 1971); *NSC 627*, 1982; *FPA H44*, 1976; *HCS 1980*, 866
RSC Lab. Hazard Data Sheet No. 22, 1984

1. Bond, J., *Loss Prev. Bull.*, 1985, (065), 25
2. *MCA SD-37*, 1971
3. Harmon, 1974, 2.17

4. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

The autocatalytic exothermic polymerisation reaction exhibited by styrene was involved in a plant-scale incident where accidental heating caused violent ejection of liquid and vapour from a storage tank [1]. Polymerisation becomes self-sustaining above 95°C [2]. The monomer has been involved in several plant-scale explosions, and must be stored at below 32°C, and for less than 3 months [3]. Styrene is a moderately endothermic compound (ΔH_f° (l) +147.7 kJ/mol, 1.42 kJ/g), and the energy of decomposition (110—300°C) has been measured as 0.67 kJ/g [4].

See other ENDOTHERMIC COMPOUNDS

Air, Polymerising styrene

Cullis, C. F. *et al., Combust. Flame*, 1978, **31**, 1—5

Introduction of polymerising liquid styrene into a heated styrene vapour—air mixture can, despite the temporary cooling effect, cause ignition to occur under conditions where it would not normally do so. This effect had been noted previously in plant incidents.

See other POLYMERISATION INCIDENTS

Alkali-metal—graphite compounds

Williams, N. E., private comm., 1968

Interlaminar compounds of sodium or potassium in graphite will ionically polymerise styrene (and other monomers) smoothly. The occasional explosions experienced were probably due to rapid collapse of the layer structure and release of very finely divided metal.

Butyllithium

Roper, A. N. *et al., Br. Polym. J.*, 1975, **7**, 195—203

Thermal explosion which occurred during fast anionic polymerisation of styrene, catalysed by butyllithium, was prevented by addition of low MW polystyrene before the catalyst.

See other POLYMERISATION INCIDENTS

Chlorine, Iron(III) chloride

See Chlorine: Iron(III) chloride, Monomers

Dibenzoyl peroxide

1. Sebastian, D. H. *et al., Polym. Eng. Sci.*, 1976, **16**, 117—123
2. Uchida, T. *et al., J. Chem. Eng. Jap.*, 1998, **31**(6), 960

The conditions were determined for runaway/non-runaway polymerisation of styrene in an oil-heated batch reactor at 3 bar, using dibenzoyl peroxide as initiator at 3 concentrations. Results are presented diagrammatically [1]. A calorimetric study of polymerisation initiated by benzoyl peroxide not surprisingly concluded that emulsion polymerisation in water is safer than bulk polymerisation [2].

See other POLYMERISATION INCIDENTS

Initiators

Biesenberger, J. A. *et al., Polym. Eng. Sci.*, 1976, **16**, 101—116

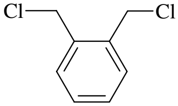
The parameters were determined in a batch reactor for thermal runaway polymerisation of styrene, initiated by azoisibutyronitrile, dibenzoyl peroxide or di-*tert*-butyl peroxide.
See other POLYMERISATION INCIDENTS

Other reactants
Yoshida, 1980, 218
MRH values calculated for 14 combinations with oxidants are given.

Oxygen MRH 9.75/73
Barnes, C. E. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 210
Exposure of unstabilised styrene to oxygen at 40—60°C generated a styrene—oxygen interpolymeric peroxide which, when isolated, exploded violently on gentle heating.
See other POLYPEROXIDES

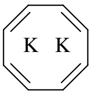
Trichlorosilane
See Trichlorosilane: Styrene
See related ALKENES

2941. 1,2-Bis(chloromethyl)benzene
[612-12-4] **$C_8H_8Cl_2$**



Catalytic impurities
Naef, H., private comm., 1980
The molten material, after holding for 4 h at 78°C in a stainless steel vessel, underwent a thermal runaway reaction and 500 kg erupted through the vent line. It was later found that addition of 0.1% of rust to the hot material led to an accelerating self-condensation Friedel-Craft reaction, catalysed by iron(III) chloride, which led to formation of poly-benzyls accompanied by evolution of hydrogen chloride.
Benzyl chloride: Catalytic impurities
See Benzyl bromide: Molecular sieve
See other BENZYL COMPOUNDS, GAS EVOLUTION INCIDENTS, POLYCONDENSATION REACTION INCIDENTS

2942. Dipotassium μ-cyclooctatetraene
[59391-85-4] **$C_8H_8K_2$**



Air, or Oxygen

1. Starks, D. F. *et al., Inorg. Chem.*, 1974, **13**, 1307
2. Evans, W. J. *et al., J. Org. Chem.*, 1981, **46**, 3927

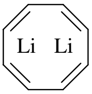
The dry solid is violently pyrophoric, exploding on contact with oxygen [1], or air [2]. The solid produced by passing oxygen into a THF solution of the potassium complex must be kept wet with solvent, as it is shock-sensitive when dry [2].
See other ORGANOMETALLICS

Europium salts

Evans, W. *et al., Polyhedron*, 1995, **14**(20/21), 2945
Reaction with europium (III) chloride or a complex thereof gave europium sandwich compounds which decomposed violently on exposure to air.

2943. Dilithium μ-cyclooctatetraene

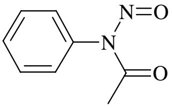
[37609-69-1] **$C_8H_8Li_2$**



Spencer, J. L., *Inorg. Synth.*, 1979, **19**, 214
The solid (but not an ether solution) is pyrophoric in air.
See other ORGANOMETALLICS

2944. *N*-Nitrosoacetanilide

[938-81-8] **$C_8H_8N_2O_2$**



Piperidine

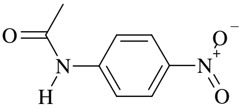
Huisgen, R., *Ann.*, 1951, **573**, 163—181
The dry anilide explodes on contact with a drop of piperidine.

Thiophene

Bamberger, E., *Ber.*, 1887, **30**, 367
A mixture prepared at 0°C exploded when removed from the cooling bath.
See other NITROSO COMPOUNDS

2945. 4-Nitroacetanilide

[104-04-1] **$C_8H_8N_2O_3$**



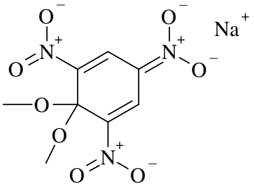
Sulfuric acid

See Sulfuric acid: Nitroaryl bases, etc.

See other NITROARYL COMPOUNDS

2946. Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide

[12275-58-0] **$C_8H_8N_3NaO_8$**



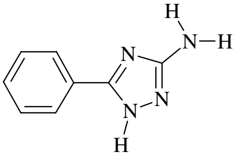
Jackson, C. L. *et al., Amer. Chem. J.*, 1898, **20**, 449

The compound is produced from interaction of trinitroanisole and sodium methoxide and explodes with great violence on heating in a free flame. It should probably be formulated as shown, a dimethyl acetal of the *aci-p*-quinonoid form of picric acid.

See other aci-NITROQUINONOID COMPOUNDS, POLYNITROARYL COMPOUNDS

2947. 5-Amino-3-phenyl-1,2,4-triazole

[4922-98-9] **$C_8H_8N_4$**



Nitrous acid

Polya, J. B., *Chem. & Ind.*, 1965, 812

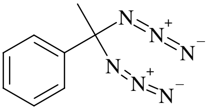
The solution, obtained by conventional diazotisation of the amine, contained some solid which was removed by filtration on a glass frit. The solid, thought to be precipitated diazonium salt (possibly an internal salt), exploded violently when disturbed with a metal spatula.

See 5-Aminotetrazole

See other DIAZOAZOLES, DIAZONIUM SALTS, TRIAZOLES

2948. 1,1-Diazidophenylethane

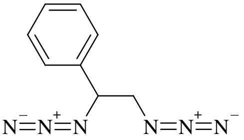
[87272-16-0] **$C_8H_8N_6$**



Kinlager, S. *et al., Synthesis*, 1983, 501

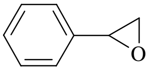
The *gem*-diazide is potentially explosive.
See other ORGANIC AZIDES

2949a. 1,2-Diazido-1-phenylethane
[22710-73-2] **$C_8H_8N_6$**



Preparative hazard
See Manganese(III) azide: Styrene
See other ORGANIC AZIDES

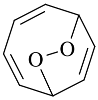
2949b. Phenyloxirane (1,2-Epoxyethylbenzene) (Styrene oxide)
[96-09-3] **C_8H_8O**



1. Anon., Personal communication, 2001
2. Editor's comments

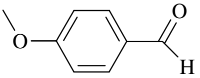
A drum of styrene oxide was punctured and the spillage absorbed into an hydrated silate absorbent, the combination swept up and drummed up for disposal. The drum became hot and started emitting copious white fumes. It was not possible to duplicate this behaviour in the laboratory unless acid or base catalyst was also present [1]. Absorbents may be inert, epoxides are not but contain considerable strain energy which will be liberated by autoreaction or nucleophilic substitution by, e.g. water. Only a catalyst is needed; neither silicates nor floor-sweepings can be guaranteed free of these [2].
See other 1,2-EPOXIDES
See SPILLAGES

2950. 7,8-Dioxabicyclo[4.2.2]-2,4,7-decatriene
[83931-97-9] **$C_8H_8O_2$**



Preparative hazard
See Oxygen (Gas): Cyclooctatetraene
See other CYCLIC PEROXIDES

2951. 4-Methoxybenzaldehyde (Anisaldehyde)
[123-11-5] $C_8H_8O_2$

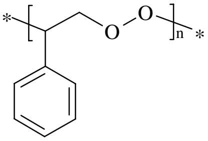


Preparative hazard

See Oxygen (Gas): 4-Methoxytoluene

See ALDEHYDES

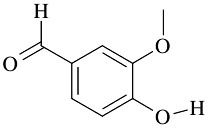
2952. Poly(styrene peroxide)
[33873-53-9] $(C_8H_8O_2)_n$



See Styrene: Oxygen

See other POLYPEROXIDES

2953. 4-Hydroxy-3-methoxybenzaldehyde (Vanillin)
[121-33-5] $C_8H_8O_3$

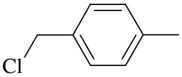


Formic acid, Thallium(III) nitrate

See Thallium(III) nitrate: Formic acid, etc.

See other ALDEHYDES

2954. 4-Methylbenzyl chloride
[104-82-5] C_8H_9Cl



Iron

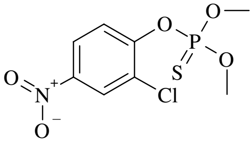
Hakl, J., *Runaway Reactions*, 1981, Paper 3/L, 4

Initial exothermic decomposition sets in at 55°C in presence of 0.02% of iron.

See other BENZYL COMPOUNDS, CATALYTIC IMPURITY INCIDENTS

2955. Dimethyl 2-chloro-4-nitrophenyl thionophosphate

[2463-84-5] **$C_8H_9ClNO_5PS$**



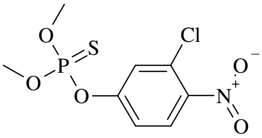
McPherson, J. B. *et al., J. Agric. Food Chem.*, 1956, **4**, 42

Thermal decomposition of a 1.5 g sample at about 270°C leads to effervescence after 20 s, with later deflagration and combustion, but a 5 g sample ignites immediately during decomposition. The induction period increases with decreasing temperature, to 384 s at 174°C. The 3-chloro analogue behaves similarly.

See other INDUCTION PERIOD INCIDENTS, PHOSPHORUS ESTERS

2956. Dimethyl 3-chloro-4-nitrophenyl thionophosphate

[500-28-7] **$C_8H_9ClNO_5PS$**

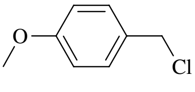


See Dimethyl 2-chloro-4-nitrophenyl thionophosphate, above

See other INDUCTION PERIOD INCIDENTS, PHOSPHORUS ESTERS

2957. 4-Methoxybenzyl chloride (Anisyl chloride)

[824-94-2] **C_8H_9ClO**



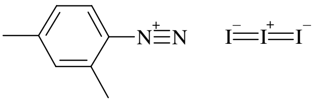
1. Bryant, R. J., personal communication 1990
2. Harger, M. J. P. *et al., J. Chem. Soc., Perk. I*, 1997, (4), 527

This compound is usually made and used in situ. A 5 g sample was allowed to sit in a screw top vial for a couple of days, one morning it was found to have blown a hole in the lid and extruded a 20ml plume of polymeric foam [1]. An attempt to dry anisyl chloride over molecular sieves pressurised the container, presumably with hydrogen chloride evolved during polymerisation [2].

See other BENZYL COMPOUNDS, POLYCONDENSATION REACTION INCIDENTS

2958. 2,4-Dimethylbenzenediazonium triiodide

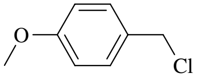
[ ] **$C_8H_9I_3N_2$**



See entry DIAZONIUM TRIIODIDES

2959. Potassium 1-phenylethanediazoate

[ ] **$C_8H_9KN_2O$**



White, E. H. *et al., J. Amer. Chem. Soc.*, 1992, **114**(221), 8023

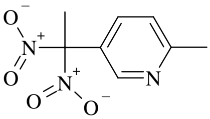
The *syn*-isomer decomposed exothermically to styrene when handled in a nitrogen atmosphere.

See other N—O COMPOUNDS

See related DIAZONIUM SALTS

2960. 5(1,1-Dinitroethyl)-2-methylpyridine

[ ] **$C_8H_9N_3O_4$**

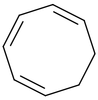


See Nitric acid: 5-Ethyl-2-methylpyridine

See other POLYNITROALKYL COMPOUNDS

2961. 1,3,5-Cyclooctatriene

[1871-52-9] **C_8H_{10}**

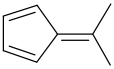


See Diethyl acetylenedicarboxylate: 1,3,5-Cyclooctatriene

See related DIENES

2962. 6,6-Dimethylfulvene

[2175-91-9] **C_8H_{10}**



Air, or Ether

Engler, C. *et al., Ber.*, 1901, **34**, 2935

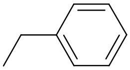
Dimethylfulvene readily peroxidised to give an insoluble (polymeric?) peroxide which exploded violently on heating to 130°C, and also caused ether used to triturate it to ignite.

See 1,4-Epidioxy-1,4-dihydro-6,6-dimethylfulvene

See other DIENES, POLYPEROXIDES

†2963. Ethylbenzene

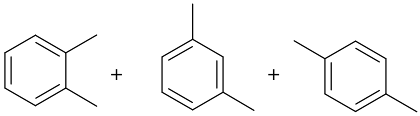
[100-41-4] **C_8H_{10}**



FPA H99, 1981; *HCS 1980*, 470; *RSC Lab. Hazards Safety Data Sheet No. 74*, 1988

†2964. *mixo*-Xylene

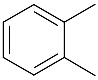
[1330-20-7] **C_8H_{10}**



NSC 204, 1968; *FPA H76*, 1978; *RSC Lab. Hazard Data Sheet No. 16*, 1983

†2965. *o*-Xylene

[95-47-6] **C_8H_{10}**



Gorecki, J. *et al., Arch. Combust.*, 1988, **8**, 123—127

The aerobic oxidation of *o*-xylene to phthalic acid or anhydride at elevated temperatures is industrially important, and the flammability limits and explosion parameters at 350°C under a range of pressures have been redetermined.

See also OXIDATION PROCESSES

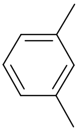
Other reactants

Yoshida, 1980, 101

MRH values calculated for 13 combinations with oxidants are given.

†2966. *m*-Xylene

[108-38-3] **C_8H_{10}**



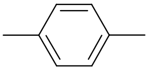
HCS 1980, 962

Sodium

See Sodium: Xylene

†2967. *p*-Xylene

[106-42-3] **C_8H_{10}**



HCS 1980, 963

Acetic acid, Air

Shraer, B. I., *Khim. Prom.*, 1970, **46**(10), 747—750

In liquid phase aerobic oxidation of *p*-xylene in acetic acid to terephthalic acid, it is important to eliminate the inherent hazards of this fuel—air mixture. Effects of temperature, pressure and presence of steam on the explosive limits of the mixture have been studied.

See OXIDATION PROCESSES

1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione

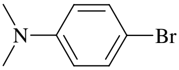
See 1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione: Xylene

Nitric acid

See Nitric acid: Hydrocarbons

2968. 4-Bromodimethylaniline

[586-77-6] **$C_8H_{10}BrN$**



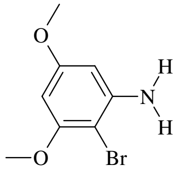
Anon., *Chem. Eng. News*, 1961, **39**(13), 37

During vacuum distillation, self-heating could not be controlled, and proceeded to explosion. Internal dehydrohalogenation to a benzyne seems a possibility.

See other HALOANILINES

2969. 2-Bromo-3,5-dimethoxyaniline

[70277-99-5] **$C_8H_{10}BrNO_2$**



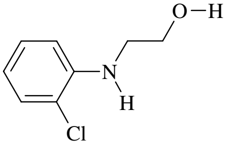
491M, 1975, 74

During laboratory-scale fractional distillation of a mixture of the aniline and its mono- and di-brominated derivatives, an explosion occurred, attributed to the lability of the bromine substituent.

See other AMINOMETHOXY COMPOUNDS, HALOANILINES

2970. 2-Chloro-*N*-(2-hydroxyethyl)aniline

[94-87-1] **$C_8H_{10}ClNO$**



CISHC Chem. Safety Summ., 1977, **48**, 25; Shaw, A. W., private comm., 1978

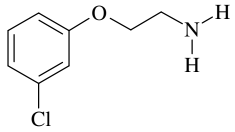
During the vacuum fractional distillation of bulked residues (7.2 t containing 30—40% of the bis(hydroxyethyl) derivative, and up to 900 ppm of iron) at 210—225°C/ 445—55 mbar in a mild steel still, a runaway decomposition set in and accelerated to explosion. Laboratory work on the material charged showed that exothermic decomposition on the large scale would be expected to set in around 210—230°C, and that the induction time at 215°C of 12—19 h fell to 6—9 h in presence of mild steel. Quantitative work in sealed tubes showed a maximum rate of pressure rise of 45 bar/s, to a maximum developed pressure of 200 bar. The thermally induced decomposition produced primary amine, hydrogen chloride, ethylene, methane, carbon monoxide and carbon dioxide.

See other GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS

See related HALOANILINES

2971. 2(3-Chlorophenoxy)ethylamine

[6488-00-2] **$C_8H_{10}ClNO$**

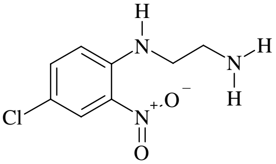


Energy of exothermic decomposition in range 270—360°C was measured as 0.27 kJ/g

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

2972. *N*-(4-Chloro-2-nitrophenyl)-1,2-diaminoethane

[59320-16-0] **$C_8H_{10}ClN_3O_2$**

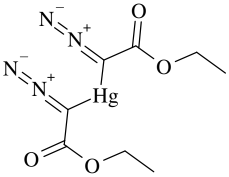


See N-(2-Nitrophenyl)-1,2-diaminoethane

See other HALOANILINES, NITROARYL COMPOUNDS

2973. Bis(ethoxycarbonyldiazomethyl)mercury

[20539-85-9] **$C_8H_{10}HgN_4O_4$**



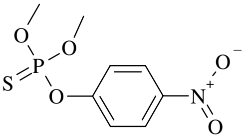
Buchner, E., *Ber.*, 1895, **28**, 217

It decomposes with foaming on melting at 104°C, and will explode under a hammer-blow.

See other DIAZO COMPOUNDS, MERCURY COMPOUNDS

2974. Dimethyl 4-nitrophenyl thionophosphate

[298-00-0] **$C_8H_{10}NO_5PS$**



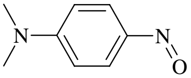
McPherson, J. B. *et al., J. Agric. Food Chem.*, 1956, **4**, 42—49

Overheating during removal of solvent by distillation from a pilot batch of ‘methyl parathion’ led to explosive decomposition, and the course of the 2-stage decomposition was studied. A 1.5 g sample immersed at 270°C decomposes after an induction period of 54 s and the residue later deflagrates, but a 5 g sample deflagrates during the initial decomposition.

See other INDUCTION PERIOD INCIDENTS, PHOSPHORUS ESTERS

2975. *N,N*-Dimethyl-4-nitrosoaniline

[138-89-6] **$C_8H_{10}N_2O$**



Energy of exothermic decomposition (in range 120—310°C) measured as 1.92 kJ/g by DSC, and T_{ait24} was determined as 87°C by adiabatic Dewar tests, with an apparent energy of activation of 123 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Acetic anhydride, Acetic acid

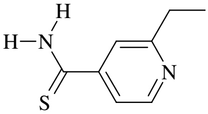
Bain, P. J. S. *et al., Chem. Brit.*, 1971, **7**, 81

An exothermic reaction, sufficiently violent to expel the flask contents, occurs after an induction period of 15—30 s when acetic anhydride is added to a solution of the nitroso compound in acetic acid. 4,4'-Azobis(*N,N*-dimethylaniline), isolated from the reaction tar, may have been formed in a redox reaction, possibly involving an oxime derived from the nitroso compound.

See other INDUCTION PERIOD INCIDENTS, NITROSO COMPOUNDS, REDOX REACTIONS

2976. 2-Ethylpyridine-4-carbothioamide

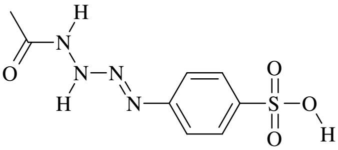
[536-33-4] **$C_8H_{10}N_2S$**



See FRICTIONAL INITIATION INCIDENTS (reference 2)

2977. 1-Acetyl-4-(4'-sulfophenyl)-3-tetrazene (4-(4-Acetyl-1-tetrazenyl)benzenesulfonic acid))

[70324-27-5] **$C_8H_{10}N_4O_4S$**



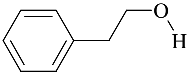
Houben-Weyl, 1965, Vol. 10.3, 740

It explodes on heating.

See other HIGH-NITROGEN COMPOUNDS, ORGANIC ACIDS, TETRAZENES

2978. Benzeneethanol (Phenethyl alcohol)

[60-12-8] **$C_8H_{10}O$**

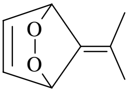


Nitric acid

See Nitric acid: Benzeneethanol, Sulfuric acid

2979. 1,4-Epidioxy-1,4-dihydro-6,6-dimethylfulvene (7-(1-Methylethylidene)-2,3-dioxabicyclo[2.2.1]hept-5-ene)

[51027-90-8] **$C_8H_{10}O_2$**



Harada, N. *et al., Chem. Lett. (Japan)*, 1973, 1173—1176

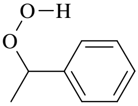
When free of solvent it decomposes explosively above —10°C.

See 6,6-Dimethylfulvene: Air, or Ether

See other CYCLIC PEROXIDES

2980. 1-Hydroperoxphenylethane

[3071-32-7] **$C_8H_{10}O_2$**



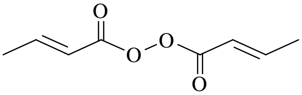
Druliner, J. D., *Chem. Eng. News*, 1981, **59**(14), 3

A 9 g sample of the freshly prepared hydroperoxide decomposed after 20 min at ambient temperature, bursting the 20 ml glass container. A 30% solution of the hydroperoxide in ethylbenzene is stable.

See other ALKYL HYDROPEROXIDES

2981. Dicrotonoyl peroxide

[93506-63-9] **$C_8H_{10}O_4$**

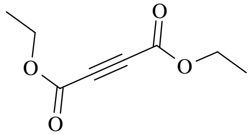


Guillet, J. E. *et al.*, Ger. Pat. 1 131 407, 1962

The diacyl peroxide and its lower homologues, though of relatively high thermal stability, are very shock-sensitive. Replacement of the hydrogen atoms adjacent to the carbonyl groups with alkyl groups renders the materials non-shock-sensitive.

See other DIACYL PEROXIDES

2982. Diethyl acetylenedicarboxylate
[762-21-0] **$C_8H_{10}O_4$**



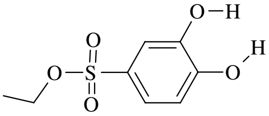
1,3,5-Cyclooctatriene

Foote, C. S., private comm., 1965

A mixture of the reactants being heated at 60°C to effect a Diels-Alder addition exploded. Onset of this vigorously exothermic reaction was probably delayed by an induction period, and presence of a solvent and/or cooling would have moderated it.

See other ACETYLENIC COMPOUNDS, INDUCTION PERIOD INCIDENTS

2983. Ethyl 3,4-dihydroxybenzenesulfonate
[ ] **$C_8H_{10}O_5S$**

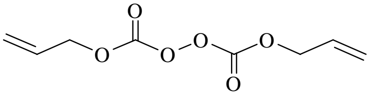


Acetyl nitrate

See Acetyl nitrate: Ethyl 3,4-dihydroxybenzenesulfonate

See other SULFUR ESTERS

2984. Diallyl peroxydicarbonate
[34037-79-1] **$C_8H_{10}O_6$**

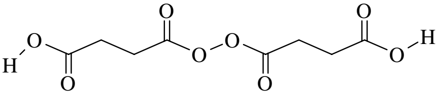


The distilled oil exploded on storage at ambient temperature.

See entry PEROXYCARBONATE ESTERS

See other ALLYL COMPOUNDS

2985. Bis(3-carboxypropionyl) peroxide
[123-23-9] **$C_8H_{10}O_8$**

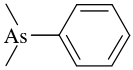


Lombard, R. *et al., Bull. Soc. Chim. Fr.*, 1963, **12**, 2800

It explodes on contact with flame. The commercial dry 95% material ('succinic acid peroxide') is highly hazard-rated.
See other COMMERCIAL ORGANIC PEROXIDES, DIACYL PEROXIDES, ORGANIC ACIDS

2986. Dimethylphenylarsine

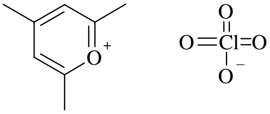
[696-26-4] **$C_8H_{11}As$**



Hydrogen peroxide
See Hydrogen peroxide: Dimethylphenylarsine
See related ALKYLNON-METALS

2987. 2,4,6-Trimethylpyrilium perchlorate

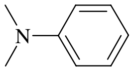
[940-93-2] **$C_8H_{11}ClO_5$**



Hafner, K. *et al., Org. Synth.*, 1964, **44**, 102
The crystalline solid is an impact- and friction-sensitive explosive and must be handled with precautions. These include use of solvent-moist material and storage in a corked rather than glass-stoppered vessel.
See other GLASS INCIDENTS, NON-METAL PERCHLORATES

2988. *N,N*-Dimethylaniline

[121-69-7] **$C_8H_{11}N$**



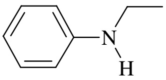
HCS 1980, 425

Dibenzoyl peroxide MRH 2.26/99+
See Dibenzoyl peroxide: *N,N*-Dimethylaniline

Diisopropyl peroxydicarbonate
See Diisopropyl peroxydicarbonate: Amines, etc.

Other reactants
Yoshida, 1980, 166
MRH values calculated for 14 combinations with oxidants are given.
See other ORGANIC BASES

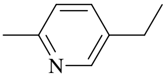
2989. *N*-Ethylaniline
[103-69-5] **$C_8H_{11}N$**



HCS 1980, 469

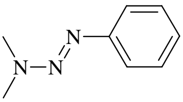
Nitric acid
See Nitric acid: Aromatic amines

2990. 5-Ethyl-2-methylpyridine
[104-90-5] **$C_8H_{11}N$**



Nitric acid
See Nitric acid: 5-Ethyl-2-methylpyridine
See other ORGANIC BASES

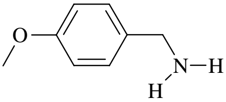
2991. 3,3-Dimethyl-1-phenyltriazene
[7227-91-0] **$C_8H_{11}N_3$**



1. Baeyer, O. *et al., Ber.*, 1875, **8**, 149
2. Heusler, F., *Ann.*, 1890, **260**, 249

It decomposes explosively on attempted distillation at ambient pressure [1], but may be distilled uneventfully at reduced pressure [2].
See other TRIAZENES

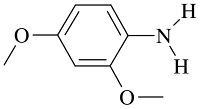
2992. 3-Methoxybenzylamine
[5071-96-5] **$C_8H_{11}NO$**



Energy of decomposition (in range 280—430°C) measured as 0.22 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AMINOMETHOXY COMPOUNDS, BENZYL COMPOUNDS

2993. 2,4-Dimethoxyaniline

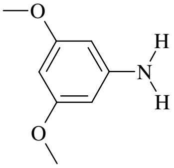
[2735-04-8] **$C_8H_{11}NO_2$**



Energy of decomposition (in range 160—440°C) measured as 0.55 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AMINOMETHOXY COMPOUNDS

2994. 3,5-Dimethoxyaniline

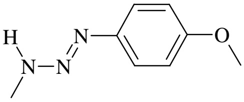
[10272-07-8] **$C_8H_{11}NO_2$**



Energy of decomposition (in range 320—450°C) measured as 0.83 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AMINOMETHOXY COMPOUNDS

2995a. 1-(4-Methoxyphenyl)-3-methyltriazene

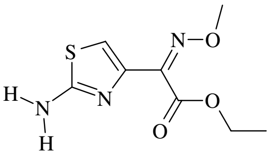
[53477-43-3] **$C_8H_{11}N_3O$**



Rondevstedt, C. S. *et al., J. Org. Chem.*, 1957, **22**, 203
The liquid product exploded on attempted vacuum distillation at below 1 mbar.
See other TRIAZENES
See related AMINOMETHOXY COMPOUNDS

2995b. Ethyl 2-(2-amino-4-thiazole)-2-methoxyiminoacetate

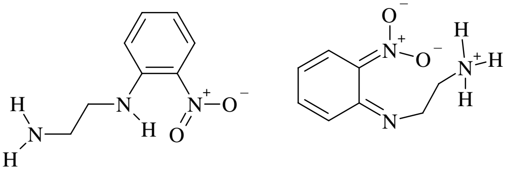
[64485-88-7] **$C_8H_{11}N_3O_3S$**



Anon. Personal communication, 2001

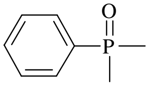
Samples of this antibiotic side-chain intermediate have been seen with manufacturers's labelling implying that it is explosive. This seems to be excessive caution. However, both it and derived compounds are exothermically unstable from temperatures around 100°C upwards, emitting considerable permanent gas. Intermediates on the usual synthesis to it are also unstable, and more energetic, up to 2 kJ/g, with exothermic decomposition of crude samples from as low as 50°C.
See OXIMES

2996. *N*-(2-Nitrophenyl)-1,2-diaminoethane
[51138-16-0] **$C_8H_{11}N_3O_2$**



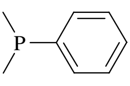
Doleschall, G. *et al., Tetrahedron*, 1976, **32**, 59
This, and the corresponding 5-chloro and 5-methoxy derivatives, tend to explode during vacuum distillation, and minimal distillation pressures and temperatures are recommended. This instability, (which was not noted for the homologues in which the hydrogen atom of the secondary amino group was replaced by alkyl) may be connected with the possibilty of isomerisation to the *aci*-nitro iminoquinone internal salt species, indicated in the reaction sequence.
See aci-NITROQUINONOID COMPOUNDS, NITROAROMATIC—ALKALI HAZARDS
See other NITROARYL COMPOUNDS

2997. Dimethylphenylphosphine oxide
[10311-08-7] **$C_8H_{11}OP$**



Preparative hazard
See Hydrogen peroxide: Dimethylphenylphosphine
See related ALKYLPHOSPHINES

2998. Dimethylphenylphosphine
[672-66-2] **$C_8H_{11}P$**



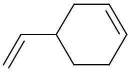
Hydrogen peroxide

See Hydrogen peroxide: Dimethylphenylphosphine

See other ALKYLPHOSPHINES

†2999. 4-Vinylcyclohexene

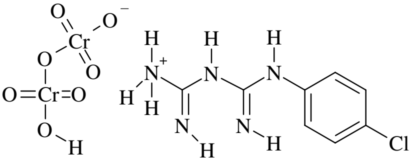
[100-40-3] **C_8H_{12}**



See other PEROXIDISABLE COMPOUNDS

3000. 1-(4-Chlorophenyl)biguanidinium hydrogen dichromate

[15842-89-4] **$C_8H_{12}ClCr_2N_5O_7$**

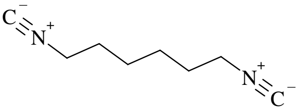


See entry DICHROMATE SALTS OF NITROGENOUS BASES

See other OXOSALTS OF NITROGENOUS BASES

3001. 1,6-Diisocyanohexane

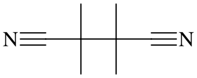
[929-57-7] **$C_8H_{12}N_2$**



See entry DIISOCYANIDE LIGANDS

3002. Tetramethylsuccinodinitrile

[3333-52-6] **$C_8H_{12}N_2$**



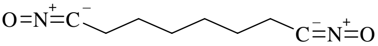
Preparative hazard

See Azoisobutyronitrile: Heptane

See other CYANO COMPOUNDS

3003. 1,6-Diisocyanatohexane

[822-06-0] **$C_8H_{12}N_2O_2$**



Alcohols

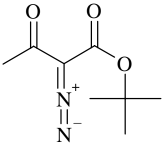
491M, 1975, 19

Base-catalysed reactions of isocyanates, such as the title compound, with alcohols may be explosively violent in absence of diluting solvents.

See other ORGANIC ISOCYANATES

3004. *tert*-Butyl 2-diazoacetoacetate

[13298-76-5] **$C_8H_{12}N_2O_3$**



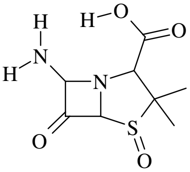
Regitz, M. *et al., Org. Synth.*, 1968, **48**, 38

During low-temperature crystallisation, scratching to induce seeding of the solution must be discontinued as soon as the sensitive solid separates.

See other DIAZO COMPOUNDS

3005. 6-Aminopenicillanic acid *S*-oxide

[4888-97-5] **$C_8H_{12}N_2O_4S$**



Preparative hazard

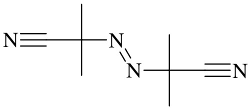
1. Micetich, R. G., *Synthesis*, 1976, **4**, 264
2. Noponen, A., *Chem. Eng. News*, 1977, **55**(8), 5
3. Micetich, R. G., *Chem. Brit.*, 1977, **13**, 163

According to a published procedure, the sulfur-containing acid is oxidised to the sulfoxide with hydrogen peroxide and precipitiated as the 4-toluenesulfonate salt in the presence of acetone [1]. During subsequent purification, trimeric acetone peroxide was precipitated and exploded violently after filtration [2]. The use of acetone in this and similar preparations involving hydrogen peroxide is not now recommended, and is highly dangerous [3].

See Hydrogen peroxide: Acetone, etc.

See also 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane

3006. Azoisobutyronitrile (AZDN)
[78-67-1] **$C_8H_{12}N_4$**



1. Lamy, P., *J. Calorim. Anal. Therm.*, 1980, **11**, 2-10-1—2-10-11
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
3. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987
4. Kilattab, M. A. *et al., Bull. Fac. Sci. Alexandria Univ.*, 1995, **35**(2), 229; *Chem. Abs.*, 1996, **124**, 184211c
5. *CHETAH*, 1990, 187
6. Gladwell, P., *Loss Prev. Bull.*, 1998, 139, 3
7. Kilattab, M. A. *et al., Chem. Abs.*, 1996, **124**, 184211c

AZDN is a much used polymerisation initiator, producing radicals and evolving nitrogen. A mathematical model of thermal dissociation leading to explosion was verified experimentally with solutions of the nitrile in dibutyl phthalate and silicone oil [1]. It shows a very high rate of pressure increase during exothermic decomposition. Energy of decomposition (78—130°C) measured by DSC as 1.3 kJ/g [2], and further work on thermal decomposition under confinement has been done [3]. The more recently calculated value of 56°C for the critical ignition temperature is in agreement with the previous value of 54°C and calorimetric studies of runaway hazards [4,7]. It is shock sensitive [5]. A review of numerous fires and explosions caused by, or involving, AZDN has been published. Several appear to have started below the 40°C temperature now required by transport regulations. Refrigeration is desirable and confinement must be avoided. Solutions are even less stable than the solid and are not normally transported or stored [6].

See BLOWING AGENTS, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

See entry CRITICAL IGNITION TEMPERATURE

Acetone

Carlisle, P. J., *Chem. Eng. News*, 1949, **27**, 150

During recrystallisation of technical material from acetone, explosive decomposition occurred. Non-explosive decomposition occurred when the nitrile was heated alone, or in presence of methanol.

Ammonium peroxodisulfate

See Ammonium peroxodisulfate: Azoisobutyronitrile

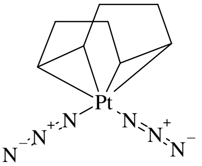
See other AZO COMPOUNDS, BLOWING AGENTS, CYANO COMPOUNDS

Heptane

Scheffold, R. *et al., Helv. Chim. Acta*, 1975, **58**, 60

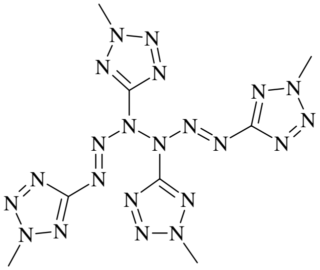
During preparation of tetramethylsuccinodinitrile by thermal decomposition of 100 g of the azonitrile by slow warming in unstirred heptane, an explosion occurred. Successive addition of small portions of the nitrile to heptane at 90—92°C is a safer, preferred method.

3007. Diazido[(1,2,5,6-η)-1,5-Cyclooctadiene]platinum
[144673-73-4] **$C_8H_{12}N_6Pt$**



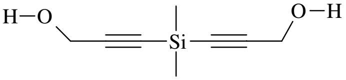
Kim, Y. *et al., Bull. Korean Chem. Soc.*, 1994, **15**(8), 690
Exploded during melting point determination.
See other AZIDES

3008a. 1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene
[83195-98-6] **$C_8H_{12}N_{22}$**



Butler, R. N. *et al., J. Chem. Res., Synop.*, 1982, 183
With 74% N content, it is explosive, sensitive to shock, friction or rapid heating to 121—125°C.
See other HIGH-NITROGEN COMPOUNDS, TETRAZOLES

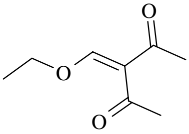
3008b. Dimethylsilyl-bis(propynol)
[233282-84-3] **$C_8H_{12}O_2Si$**



Novokshonov, V. V. *et al., Russ. J. Org. Chem.*, 1998, **34**(10), 1426
Violent polymerisation is reported during an attempt to vacuum distil this compound
See other ACETYLENIC COMPOUNDS

3009. 3-Ethoxymethylene-2,4-pentanedione

[33884-41-2] **$C_8H_{12}O_3$**

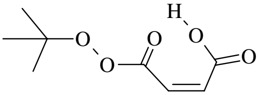


Riley, D. P. *et al., Inorg. Synth.*, 1978, **18**, 37

The residue from distillation of the title compound (prepared from ethyl orthoformate, pentanedione and acetic anhydride) at 165—170°C/13 mbar, is pyrophoric when hot.

3010. *O—O-tert*-Butyl hydrogen monoperoxymaleate

[1931-62-0] **$C_8H_{12}O_5$**



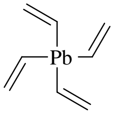
Castrantas, 1965, 17

Slightly shock-sensitive, the commercial dry 95% material is highly hazard-rated.

See other COMMERCIAL ORGANIC PEROXIDES, PEROXYESTERS

3011. Tetravinyllead

[866-87-5] **$C_8H_{12}Pb$**



Holliday, A. K. *et al., Chem. & Ind.*, 1968, 1699

In the preparation from lead(II) chloride and vinylmagnesium bromide in THF—hexane, violent explosions occurred during isolation of the product by distillation of solvent. This could be avoided by a procedure involving steam distillation of the tetravinyllead, no significant loss of yield by hydrolysis being noted. It is likely to be considerably more endothermic than tetraethyllead.

Diborane

See Diborane: Tetravinyllead

Phosphorus trichloride

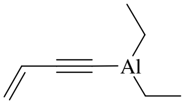
Houben-Weyl 1975, Vol. 13.3, 244

In absence of solvent, interaction may be explosive

See related ALKYLMETALS, ENDOTHERMIC COMPOUNDS

3012. 3-Buten-1-ynyldiethylaluminium

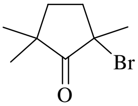
[ ] **$C_8H_{13}Al$**



Petrov, A. A. *et al., Zh. Obsch. Khim.*, 1962, **32**, 1349
It ignites in air.
See other METAL ACETYLIDES, TRIALKYLALUMINIUMS

3013. 2-Bromo-2,5,5-trimethylcyclopentanone

[69167-99-3] **$C_8H_{13}BrO$**

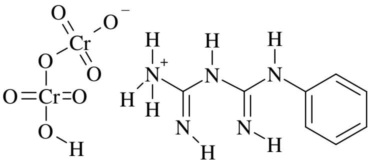


Potassium hydroxide, Triethylene glycol

Adam, W., *J. Amer. Chem. Soc.*, 1986, **108**, 4559
In the preparation of 2,5,5-trimethylcyclopenten-3-one by dehydrobromination of the title bromoketone, the scale should be limited to below 10 g of the latter, to avoid a vigorous exotherm and loss of control on addition of the bromoketone to potassium hydroxide in triethylene glycol at 60—70°C.
See related HALOALKANES

3014. 1-Phenylbiguanidinium hydrogen dichromate

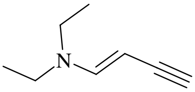
[15760-45-9] **$C_8H_{13}Cr_2N_5O_7$**



See entry DICHROMATE SALTS OF NITROGENOUS BASES
See other OXOSALTS OF NITROGENOUS BASES

3015. 1-Diethylamino-1-buten-3-yne

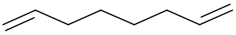
[1809-53-6] **$C_8H_{13}N$**



Brandsma, 1971, 163

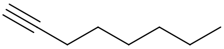
Dilution of the amine with white mineral oil is recommended before vacuum distillation, to avoid explosive decomposition of the residue.
See other ACETYLENIC COMPOUNDS

†3016. 1,7-Octadiene
[3710-30-3] **C_8H_{14}**



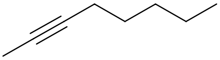
See other DIENES

†3017. 1-Octyne
[629-05-0] **C_8H_{14}**



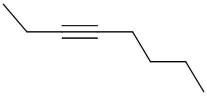
See other ALKYNES

†3018. 2-Octyne
[2809-67-8] **C_8H_{14}**



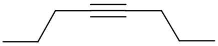
See other ALKYNES

†3019. 3-Octyne
[15232-76-5] **C_8H_{14}**



See other ALKYNES

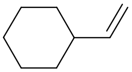
†3020. 4-Octyne
[1942-45-6] **C_8H_{14}**



See other ALKYNES

†3021. Vinylcyclohexane

[695-12-5] **C_8H_{14}**



See related ALKENES

3022. Di-2-butenylcadmium

[7544-40-3] **$C_8H_{14}Cd$**

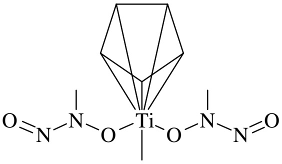
Houben-Weyl, 1973, Vol. 13.2a, 881

When rapidly warmed from —5°C to ambient temperature, it decomposes explosively.

See related ALKYLMETALS, ALLYL COMPOUNDS

3023. *μ*-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino)titanium

[58659-15-7] **$C_8H_{14}N_4O_4Ti$**



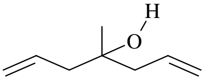
Clark, R. J. H. *et al., J. Chem. Soc., Dalton Trans.*, 1974, 122

The complex was stable under nitrogen or vacuum, but exploded quite readily and decomposed in air.

See other NITROSO COMPOUNDS, N—O COMPOUNDS, ORGANOMETALLICS

3024. 4-Hydroxy-4-methyl-1,6-heptadiene

[25201-40-5] **$C_8H_{14}O$**



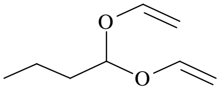
Ozone

1. Rabinowitz, J. L., *Biochem. Prep.*, 1958, **6**, 25
2. Miller, F. W., *Chem. Eng. News*, 1973, **51**(6), 29

Following a published procedure [1], but using 75 g of diene instead of the 12.6 g specified, the ozonisation product exploded under desiccation. Eight previous preparations on the specified scale had been uneventful.

See OZONIDES

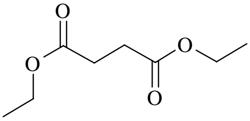
3025. Poly(vinyl butyral)
[63148-65-2] **$(C_8H_{14}O_2)_n$**



Korshova, I. T. *et al., Chem. Abs.*, 1983, **99**, 195868

Ignition and autoignition temperatures, lower explosion limit and oxygen index were determined for the powdered butyral in relation to dispersibilty and viscosity.

3026. Diethyl succinate
[123-25-1] **$C_8H_{14}O_4$**

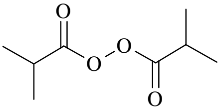


HCS 1980, 405

Ethyl trifluoroacetate, Sodium hydride

See Sodium hydride: Diethyl succinate, etc.

3027. Diisobutyryl peroxide
[3437-84-1] **$C_8H_{14}O_4$**

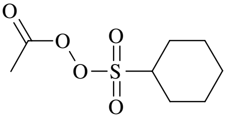


1. Kharasch, S. *et al., J. Amer. Chem. Soc.*, 1941, **63**, 526
2. *MCA Case History No. 579*

A sample of the peroxide in ether, prepared according to a published procedure [1], was being evaporated to dryness with a stream of air when it exploded violently. Handling the peroxide as a dilute solution at low temperature is recommended [2].

See other DIACYL PEROXIDES

3028. Acetyl cyclohexanesulfonyl peroxide
[3179-56-4] **$C_8H_{14}O_5S$**

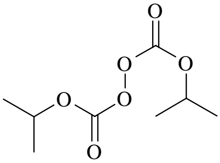


1. ‘Code of Practice for Storage of Organic Peroxides’, GC14, Widnes, Interox Chemicals Ltd, 1970
2. *CHETAH*, 1990, 182

While the commercial material damped with 30% water is not shock- or friction-sensitive, if it dries out it may become a high-hazard material. As a typical low-melting diacyl peroxide, it may be expected to decompose vigorously or explosively on slight heating or on mechanical initiation [1]. It is shock sensitive (presumably when dry) [2].

See other COMMERCIAL ORGANIC PEROXIDES, DIACYL PEROXIDES

3029. Diisopropyl peroxydicarbonate
[105-64-6] **$C_8H_{14}O_6$**



1. Strong, W. A., *Ind. Eng. Chem.*, 1964, **56**(12), 33
2. ‘Bulletin T. S. 350’, Pittsburgh, Pittsburgh Plate Glass Co., 1963

When warmed slightly above its m.p., 10°C, the ester undergoes slow but self-accelerating decomposition, which may become dangerously violent under confinement. Bulk solutions of the peroxyester (45%) in benzene—cyclohexane stored at 5°C developed sufficient heat to decompose explosively after 1 day, and 50—90% solutions were found to be impact-sensitive [1]. The solid is normally stored and transported at below —18°C in loose-topped trays [2].

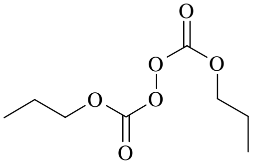
Amines, or Potassium iodide

Strain, F., *J. Amer. Chem. Soc.*, 1950, **72**, 1254

At 20—30°C, decomposition occurred in 10—30 min. Addition of 1% of aniline, 1,2-diaminoethane or potassium iodide caused instant decomposition, and of dimethylaniline, instant explosion.

See other COMMERCIAL ORGANIC PEROXIDES, DIACYL PEROXIDES, PEROXYCARBONATE ESTERS

3030. Dipropyl peroxydicarbonate
[16066-38-9] **$C_8H_{14}O_6$**



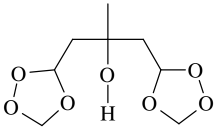
Barter, J. A., US Pat. 3 775 341, 1973

Methylcyclohexane is a suitable solvent to reduce the hazardous properties of the peroxyester.

See other DIACYL PEROXIDES, PEROXYCARBONATE ESTERS

3031. 4-Hydroxy-4-methyl-1,6-heptadiene diozonide

[ ] **$C_8H_{14}O_7$**

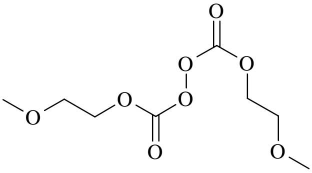


See 4-Hydroxy-4-methyl-1,6-heptadiene: Ozone

See other OZONIDES

3032. Bis(2-methoxyethyl) peroxydicarbonate

[22575-95-7] **$C_8H_{14}O_8$**

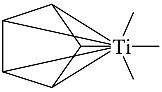


It exploded at 34°C.

See entry PEROXYCARBONATE ESTERS

3033. *μ*-Cyclopentadienyltrimethyltitanium

[38386-55-9] **$C_8H_{14}Ti$**



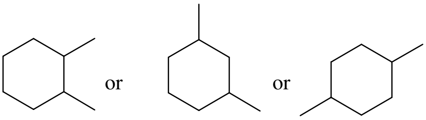
Bailar, 1973, Vol. 3, 395

Pyrophoric at ambient temperature.

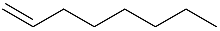
See other ALKYLMETALS, ORGANOMETALLICS

†3034. Dimethylcyclohexanes

[27195-67-1] **C_8H_{16}**

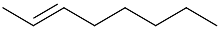


†3035. 1-Octene
[111-66-0] **C_8H_{16}**



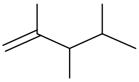
See other ALKENES

†3036. 2-Octene
[111-67-1] **C_8H_{16}**



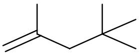
See other ALKENES

†3037. 2,3,4-Trimethyl-1-pentene
[565-76-4] **C_8H_{16}**



See other ALKENES

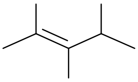
†3038. 2,4,4-Trimethyl-1-pentene
[107-39-1] **C_8H_{16}**



HCS 1980, 414

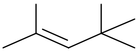
See other ALKENES

†3039. 2,3,4-Trimethyl-2-pentene
[565-77-5] **C_8H_{16}**



See other ALKENES

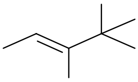
†3040. 2,4,4-Trimethyl-2-pentene
[107-40-4] **C_8H_{16}**



See other ALKENES

†3041. 3,4,4-Trimethyl-2-pentene

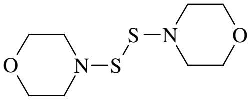
[598-96-9] **C_8H_{16}**



See other ALKENES

3042. 4,4′-Dithiodimorpholine

[103-34-4] **$C_8H_{16}N_2O_2S_2$**

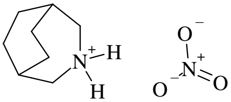


Chlorine

See 4-Morpholinesulfenyl chloride

3043. 3-Azoniabicyclo[3.2.2]nonane nitrate

[10308-93-7] **$C_8H_{16}N_2O_3$**



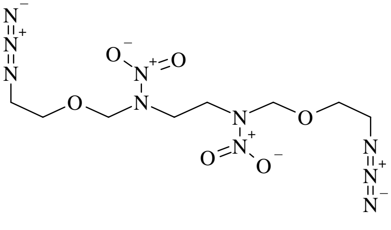
Violent decomposition at 258°C.

See entry DIFFERENTIAL THERMAL ANALYSIS

See other OXOSALTS OF NITROGENOUS BASES

3044. 1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane

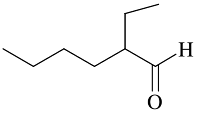
[88487-88-7] **$C_8H_{16}N_{10}O_6$**



See entry ENERGETIC COMPOUNDS

See other N—NITRO COMPOUNDS, ORGANIC AZIDES

†3045. 2-Ethylhexanal
[123-05-7] **$C_8H_{16}O$**



HCS 1980, 489

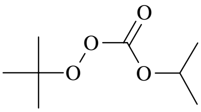
1. Steele, A. B. *et al., Chem. Engrg.*, 1969, **66**, 160
2. Urben, P. G., private comm., 1989

The aldehyde ignited in air [1]. This is typical of mid-range aldehydes if sorbed on paper or cloth which increases surface exposure, ignition occurring within 2 hours [2].

See α-Pentylcinnamaldehyde

See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

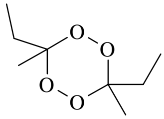
3046. *O—O-tert*-Butyl isopropyl monoperoxycarbonate
[2372-21-6] **$C_8H_{16}O_4$**



See entry THERMAL EXPLOSIONS

See other PEROXYCARBONATE ESTERS

3047. 3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane
[33817-92-4] **$C_8H_{16}O_4$**

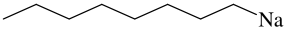


1. Castrantas, 1965, 18
2. Swern, 1970, Vol. 1, 37
3. Ho, T-C. *et al., Process Safety Progr.*, 1998, **17**(4), 259
4. Rogers, B. Internet, 1999
5. Shu, C-M. *et al., Chem. Abs.*, 2002, **136**, 325171b

By analogy, this dimeric 2-butanone peroxide and the corresponding trimer probably contribute largely to the high shock-sensitivity of the commercial ‘MEK peroxide’ mixture, which contains these and other peroxides [1,2]. MEK peroxide has featured in several very serious explosions, with scores of fatalities, in the far east. Regulations now permit storage of only limited quantities, the USA restricts it to 20 litre containers [3]. A consignment of six year old material, transported in a truck through a hot

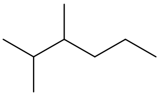
day, combusted spontaneously in the early hours of the next morning, after it should have had time to cool [4]. A study of thermal stability of solutions, with a mind to vent sizing, is abstracted [5].
See Bis(2-hydroperoxy-2-butyl) peroxide
See other CYCLIC PEROXIDES, KETONE PEROXIDES

3048. Octylsodium
[2875-36-7] **$C_8H_{17}Na$**

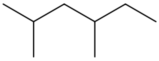


Houben-Weyl, 1970, Vol. 13.1, 384
The powder ignites in air.
See other ALKYLMETALS

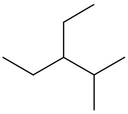
†3049. 2,3-Dimethylhexane
[584-94-1] **C_8H_{18}**



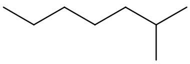
†3050. 2,4-Dimethylhexane
[589-43-5] **C_8H_{18}**



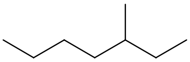
†3051. 3-Ethyl-2-methylpentane
[609-26-7] **C_8H_{18}**



†3052. 2-Methylheptane
[592-27-8] **C_8H_{18}**



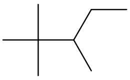
†3053. 3-Methylheptane
[589-81-1] **C_8H_{18}**



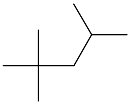
†3054. Octane
[111-65-9] **C_8H_{18}**

HCS 1980, 696

†3055. 2,2,3-Trimethylpentane
[564-02-3] **C_8H_{18}**

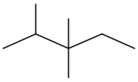


†3056. 2,2,4-Trimethylpentane
[540-84-1] **C_8H_{18}**

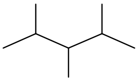


HCS 1980, 696

†3057. 2,3,3-Trimethylpentane
[560-21-4] **C_8H_{18}**

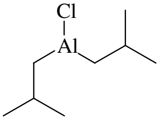


†3058. 2,3,4-Trimethylpentane
[565-75-3] **C_8H_{18}**



3059. Diisobutylaluminium chloride

[1779-25-5] **$C_8H_{18}AlCl$**

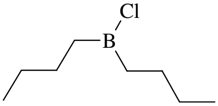


HCS 1980, 411

See entry ALKYLALUMINIUM HALIDES

3060. Chlorodibutylborane

[1730-69-4] **$C_8H_{18}BCl$**

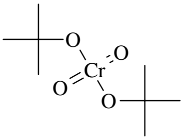


491M, 1975, 146

It ignites in air.
See other ALKYLHALOBORANES

3061. Di-*tert*-butyl chromate

[1189-85-1] **$C_8H_{18}CrO_4$**



1. Anon., *ABCM Quart. Safety Summ.*, 1953, **24**, 2
2. Koenst, W. M. B. *et al., Synth. Comm.*, 1980, **10**, 905—909

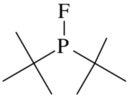
Large-scale preparation by addition of *tert*-butanol to chromium trioxide in a full unstirred flask with poor cooling detonated owing to local overheating. Effective cooling and stirring are essential [1]. It may safely be prepared by addition of a 40% aqueous solution of chromium trioxide to the alcohol [2].

Valencene

1. Hunter, G. L. K. *et al., J. Food Sci.*, 1965, **30**, 876
2. Wilson, C. W. *et al., J. Agric. Food Chem.*, 1978, **26**, 1430—1432

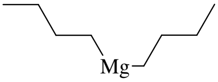
Oxidation of the sesquiterpene valencene to the 4-en-3-one proceeds explosively when at sub-ambient temperatures [1]. A safer alternative oxidation procedure is detailed [2].
See other OXIDANTS

3062. Di-*tert*-butylfluorophosphine
[29146-24-5] **$C_8H_{18}FP$**



Stelzer, O. *et al., Inorg. Synth.*, 1978, **18**, 176
It may ignite in air.
See other ALKYLHALOPHOSPHINES

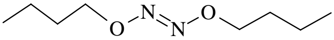
3063. Dibutylmagnesium
[1191-47-5] **$C_8H_{18}Mg$**



491M, 1975, 147

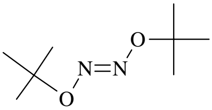
It ignites in air.
See other ALKYLMETALS

3064. Dibutyl hyponitrite
[86886-17-1] **$C_8H_{18}N_2O_2$**



See entry DIALKYL HYPONITRITES

3065a. *trans*-Di-*tert*-butyl hyponitrite
[14976-54-6] **$C_8H_{18}N_2O_2$**



Mendenhall, G. D. *et al., J. Amer. Chem. Soc.*, 1982, **104**, 5113
It is unstable and shock-sensitive, and needs careful handling.

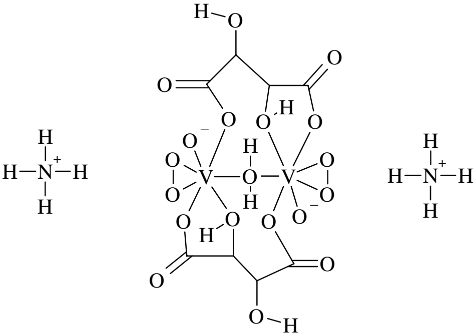
Formamides
Protasiewicz, J. *et al., J. Org. Chem.*, 1985, **50**, 3222
An equimolar mixture with *N*-*tert*-butylformamide underwent a sudden exotherm after placing in a bath at 60°C and the tube contents were ejected vigorously as a

small cloud. A 1:2 mixture of the ester with formamide emitted a loud pop on heating in a bath at 70°C.

See other DIALKYL HYPONITRITES

3065b. Diammonium Aquabis(peroxotartratovanadate)(2-)

[ ] $C_8H_{18}N_2O_{19}V_2$



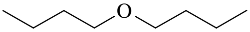
Schwendt, P, *et al., Polyhedron*, 1998, **17**(13-14), 2161

This compound, which exists as a pentahydrate and for which a considerably weirder structure than shown has been inferred from X-ray crystallography on a homologue, may decompose explosively at room temperature. Handling more than 20 mg is discountenanced.

See related PEROXO- TRANSITION METAL COMPOUNDS, PEROXOCHROMIUM COMPOUNDS

†3066. Dibutyl ether

[142-96-1] $C_8H_{18}O$



HCS 1980, 369

Dasler, W. *et al., Ind. Eng. Chem. (Anal. Ed.)*, 1946, **18**, 52

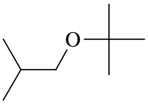
Peroxides formed in storage are removed effectively by percolation through alumina.

See ETHERS, PEROXIDES IN SOLVENTS

See other PEROXIDISABLE COMPOUNDS

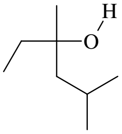
3067. 1-(1,1-Dimethylethoxy)-2-methylpropane (*tert*-Butyl isobutyl ether)

[33021-02-2] $C_8H_{18}O$



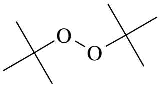
Bowen, R. D. *et al., J. Chem. Soc. Perk. 2*, 1990, 147
Despite testing negative for peroxides, a sample exploded during distillation. Precautions are recommended.
See other ETHERS, PEROXIDISABLE COMPOUNDS

3068. 3,5-Dimethyl-3-hexanol
[4209-91-0] **$C_8H_{18}O$**



Hydrogen peroxide, Sulfuric acid
See Hydrogen peroxide: 3,5-Dimethyl-3-hexanol, etc.

†3069. Di-*tert*-butyl peroxide
[110-05-4] **$C_8H_{18}O_2$**



HCS 1980, 370

1. Griffiths, J. F. *et al., Combust. Flame*, 1984, **56**, 135—148
2. Stull, 1977, 21
3. Sime, R. J., *Chem. Eng. News*, 1988, **66**(24), 4
4. Antrim, R. F. *et al. Process Safety Progr.*, 1998, **17**(3), 225

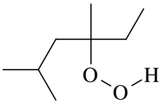
Thermal decomposition is exothermic and self-ignition may result, especially if oxygen is present [1]. Though the heat of exothermic decomposition (1.32 kJ/g) is not exceptionally high, the weakness of the peroxide link tends to ready decomposition, and the energy release, coupled with the high volume of gaseous products (7.6 mol) at the adiabatic maximum of 550°C would give a 21-fold pressure increase in a closed vessel [2]. A routine student experiment on the gas-phase decomposition of the peroxide (0.2 ml) by injection into a 250 ml flask immersed in an oil bath at 155°C. The procedure was identical to a published method except that a mercury manometer was used to measure the pressure in place of a Bourdon gauge, and the procedure had been used on 30 occasions without incident. During a run at 165°C a violent explosion occurred [3]. An explosion and fire in an earthed drum of Di-t-butyl peroxide led to an investigation which showed the material unlikely to have ignited in the drum (open cup flash point 18°C). Evidence was gained for an initial fire external to the drum leading to local overheating and thermal decomposition of the contents. Self Accelerating Decomposition Temperature is 80°C [4].
See THERMAL EXPLOSIONS
See other DIALKYL PEROXIDES, SELF-HEATING AND IGNITION INCIDENTS

Preparative hazard

See Hydrogen peroxide: *tert*-Butanol, etc.

3070. 3,5-Dimethyl-3-hexyl hydroperoxide

[ ] **$C_8H_{18}O_2$**



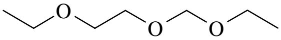
Preparative hazard

See Hydrogen peroxide: 3,5-Dimethyl-3-hexanol, etc.

See other ALKYL HYDROPEROXIDES

†3071. Bis(2-ethoxyethyl) ether

[112-36-7] **$C_8H_{18}O_3$**

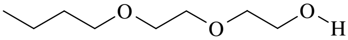


HCS 1980, 398

See other PEROXIDISABLE COMPOUNDS

†3072. 2-(2-Butoxyethoxy)ethanol (Diethyleneglycol monobutyl ether)

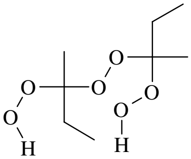
[112-34-5] **$C_8H_{18}O_3$**



HCS 1980, 231

3073. Bis(2-hydroperoxy-2-butyl) peroxide
(Dioxybis(1-methylpropyl hydroperoxide))

[126-76-1] **$C_8H_{18}O_6$**



1. Leleu, *Cahiers*, 1973, (71), 238
2. Kelley, K., www.ehs.umaryland.edu, 1997

The triperoxide, the main constituent of 'MEK peroxide', is explosive in the pure state, but insensitive to shock as the commercial 50% solution in dimethyl phthalate. The solution will explode at about 85°C, and slowly liberates oxygen at ambient temperature [1]. A seventeen year old container of MEK peroxide was discovered, the contents were placed in bowls, presumably in the hope it would evaporate. Some hours later an explosion and fire resulted. Any evaporation of volatiles would merely concentrate peroxides [2].

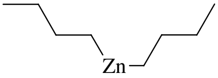
See 3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane

See other COMMERCIAL ORGANIC PEROXIDES, KETONE PEROXIDES

See related ALKYL HYDROPEROXIDES

3074. Dibutylzinc

[1119-90-0] **$C_8H_{18}Zn$**



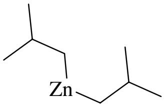
Leleu, *Cahiers*, 1977, (88), 371

It fumes in air, and may ignite under warm conditions.

See other ALKYLMETALS, DIALKYLZINCS

3075. Diisobutylzinc

[1854-19-9] **$C_8H_{18}Zn$**



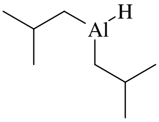
Gibson, 1969, 180

It ignites in air.

See other ALKYLMETALS, DIALKYLZINCS

3076. Diisobutylaluminium hydride

[1191-15-7] **$C_8H_{19}Al$**



1. Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **53**(1), 54A
2. 'Specialty Reducing Agents', Brochure TA-2002/1, New York, Texas Alkyls, 1971

The higher thermal stability of dialkylaluminium hydrides over the corresponding trialkylaluminiums is particularly marked in this case with 2 branched alkyl groups [1]. Used industrially as a powerful reducant, it is supplied as a solution in hydrocarbon solvents. The undiluted material ignites in air unless diluted to below 25% concentration [2].

Tetrahydrofuran

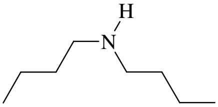
Wissink, H. G., *Chem. Eng. News*, 1997, **75**(9), 6

The reagent can react with this solvent to give gaseous byproducts, capable of bursting glass containers. Initial complex formation is exothermic, so good cooling is needed to prevent decomposition when solutions are prepared, they should not be stored.

See other ALKYLALUMINIUM ALKOXIDES AND HYDRIDES, REDUCANTS

3077. Dibutylamine

[111-92-2] **$C_8H_{19}N$**



HCS 1980, 367

Cellulose nitrate MRH 4.81/99+

See CELLULOSE NITRATE: Amines

Other reactants

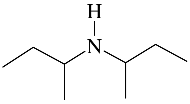
Yoshida, 1980, 163

MRH values calculated for 14 combinations with oxidants are given.

See other ORGANIC BASES

†3078. Di-2-butylamine

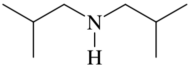
[626-23-3] **$C_8H_{19}N$**



See other ORGANIC BASES

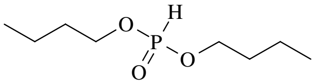
†3079. Diisobutylamine

[110-96-3] **$C_8H_{19}N$**



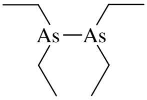
See other ORGANIC BASES

3080. Dibutyl hydrogen phosphite
[1809-19-4] **$C_8H_{19}O_3P$**



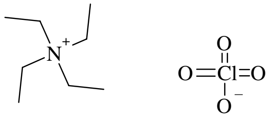
Morrell, S. H., private comm., 1968
The phosphite was being distilled under reduced pressure. At the end of distillation the air-bleed was opened more fully, when spontaneous combustion occurred inside the flask, probably of phosphine formed by thermal decomposition.
See other PHOSPHORUS ESTERS

3081. Tetraethyldiarsane
[612-08-8] **$C_8H_{20}As_2$**



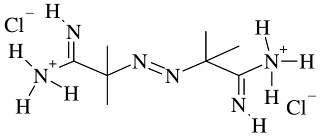
Sidgwick, 1950, 770
It ignites in air.
See other ALKYLNON-METALS

3082. Tetraethylammonium perchlorate
[2567-83-1] **$C_8H_{20}ClNO_4$**



Udupa, M. R., *Propellants, Explos. Pyrotech.*, 1982, **7**, 155—157
It explodes at 298°C after an energetic phase transformation (10.4 kJ/mol) at 98°C.
See other PERCHLORATE SALTS OF NITROGENOUS BASES, QUATERNARY OXIDANTS

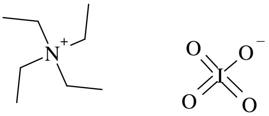
3083. 2,2′-Azobis(2-amidiniopropane) chloride
[2997-92-4] **$C_8H_{2}0Cl_2N_6$**



Sodium peroxodisulfate
See 2,2’-Azobis(2-amidiniopropane) peroxodisulfate
See other AZO COMPOUNDS, POLYMERISATION INCIDENTS

3084. Tetraethylammonium periodate

[5492-69-3] **$C_8H_{20}INO_4$**



Preparative hazard

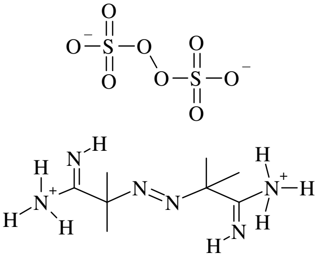
See Periodic acid: Tetraethylammonium hydroxide

See also Tetramethylammonium periodate

See other OXOSALTS OF NITROGENOUS BASES, QUATERNARY OXIDANTS

3085. 2,2′-Azobis(2-amidiniopropane) peroxodisulfate

[ ] **$C_8H_{20}N_6O_8S_2$**



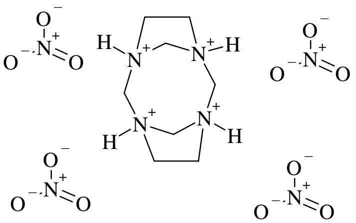
Rausch, D. A., *Chem. Eng. News*, 1988, **66**(5), 2

When aqueous solutions of the polymerisation initiators 2,2’-azobis(2-amidiniopropane) chloride and sodium peroxodisulfate are mixed, the title compound separates as a water insoluble shock-sensitive salt. The shock-sensitivity increases as the moisture level decreases, and is comparable with that of lead azide. Stringent measures should be used to prevent contact of the solutions outside the polymerisation environment. (The instability derives from the high nitrogen (21.4%) and oxygen (31.6%) contents, and substantial oxygen balance, as well as the structural factors present in the salt.)

See other AZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

3086. 1,3,6,8-Tetraazatricyclo[6.2.1.1^{3,6}]dodecane tetranitrate

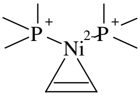
[10308-95-9] **$C_8H_{20}N_8O_{12}$**



Violent decomposition occurred at 260°C.

See entry DIFFERENTIAL THERMAL ANALYSIS (DTA) *See other* OXOSALTS OF NITROGENOUS BASES

3087. Bis(trimethylphosphine)nickel(0)—acetylene complex
[98316-02-0] **$C_8H_{20}NiP_2$**

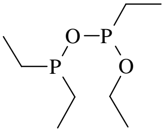


Pörschke, K. R. *et al., Z. Naturforsch. B*, 1985, **40B**, 199—209

The complex with acetylene (1 mol) decomposed explosively at 0°C.

See related ALKYLPHOSPHINES, COMPLEX ACETYLIDES

3088. Ethoxytriethyldiphosphinyl oxide
[114328-89-1] **$C_8H_{20}O_2P_2$**

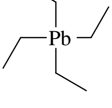


491M, 1975, 167

It ignites in air.

See related ALKYLPHOSPHINES

3089. Tetraethyllead
[78-00-2] **$C_8H_{20}Pb$**



HCS 1980, 890

Doyle, F. P., *Loss Prev.*, 1969, **3**, 16

It is mildly endothermic (ΔH_f° (l) +217.5 kJ/mol, 0.56 kJ/g).

Failure to cover the residue with water after emptying a tank of the compound caused explosive decomposition after several days.

Other reactants

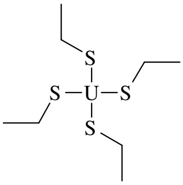
Yoshida, 1980, 234

MRH values calculated for 12 combinations with oxidants are given.

See other ALKYLMETALS, ENDOTHERMIC COMPOUNDS

3090. Tetrakis(ethylthio)uranium

[ ] **$C_8H_{20}S_4U$**



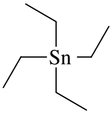
Bailar, 1973, Vol. 5, 416

It ignites in air.

See related METAL ALKOXIDES

3091. Tetraethyltin

[597-64-8] **$C_8H_{20}Sn$**



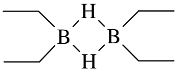
Sorbe, 1968, 160

It tends to ignite in air.

See other ALKYLMETALS

3092. 'Tetraethyldiborane'

[12081-54-8] **$C_8H_{22}B_2$**



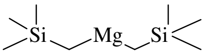
Köster, R. *et al., Inorg. Synth.*, 1974, **15**, 141—146

The material (actually an equilibrium mixture of diborane and highly ethylated homologues) ignites in air. The propyl analogue behaves similarly.

See other ALKYLBORANES

3093. Bis(trimethylsilylmethyl)magnesium

[51329-17-0] **$C_8H_{22}MgSi_2$**



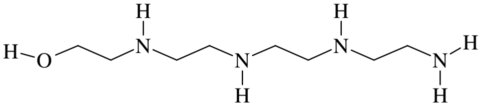
Oxygen, or Water

Andersen, R. A. *et al., Inorg. Synth.*, 1979, **19**, 264

It is sensitive to oxygen and reacts violently with water.

See related ALKYLMETALS, ALKYLSILANES

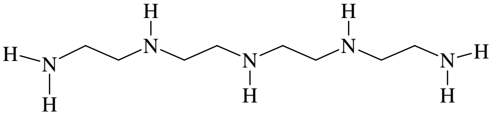
3094. 3,6,9-Triaza-11-aminoundecanol (‘Hydroxyethyltriethylenetetramine’)
[38361-85-2] **$C_8H_{22}N_4O$**



HCS 1980, 889

Cellulose nitrate
See CELLULOSE NITRATE: Amines
See other ORGANIC BASES

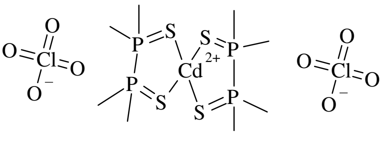
3095. 1,11-Diamino-3,6,9-triazaundecane (‘Tetraethylenepentamine’)
[112-57-2] **$C_8H_{23}N_5$**



Carbon tetrachloride
See Carbon tetrachloride: 1,11-Diamino-3,6,9-triazaundecane

Cellulose nitrate
See CELLULOSE NITRATE: Amines
See other ORGANIC BASES

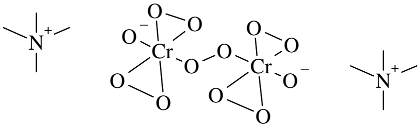
3096. Bis(tetramethyldiphosphane disulfide)cadmium perchlorate
[71231-59-9] **$C_8H_{24}CdCl_2O_8P_4S_4$**



McQuillan, G. P. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 899
This and the nickel analogue are shock-sensitive and violently explosive. Other metal complexes (except cobalt) decompose slowly liberating the dimethyldiphosphane which tends to ignite when old sample bottles are opened.
See related AMMINEMETAL OXOSALTS

3097. Tetramethylammonium pentaperoxodichromate

[ ] **$C_8H_{24}Cr_2N_2O_{12}$**



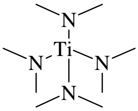
Mellor, 1943, Vol. 11, 358

The structure given is a 1960's vintage re-interpretation of the salt of CrO_5^- given by Mellor.

See Tetramethylammonium monoperchromate

3098. Tetrakis(dimethylamino)titanium

[ ] **$C_8H_{24}N_4Ti$**



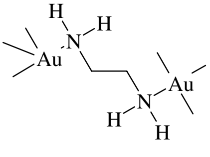
Hydrazine

See Hydrazine: Titanium compounds

See other N-METAL DERIVATIVES

3099. 1,2-Diaminoethanebis(trimethylgold)

[ ] **$C_8H_{26}Au_2N_2$**



Alone, or Nitric acid

Gilman, H. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 550

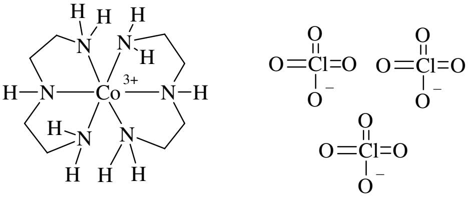
The solid complex is very sensitive to light and explodes violently on heating in an open crucible. A drop of conc. nitric acid added to the dry compound causes explosion.

See other GOLD COMPOUNDS

See related ALKYLMETALS

3100a. Bis(diethylenetriamine)cobalt(III) perchlorate

[28872-17-5] **$C_8H_{26}Cl_3CoN_6O_{12}$**

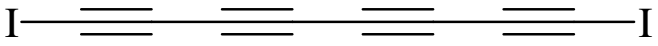


It explodes at 325°C; high impact-sensitivity.

See entry AMMINEMETAL OXOSALTS

3100b. Diiodooctatetrayne

[301831-81-1] **C_8I_2**



Gao, K. *et al., J. Amer. Chem. Soc.*, 2000, **122**(38), 9320

Explodes above 85°C during melting point determination.

See other HALOACETYLENE DERIVATIVES

3101. Potassium graphite

[12081-88-8] **C_8K**

KC_8

Water

Bailar, 1973, Vol. 1, 1276

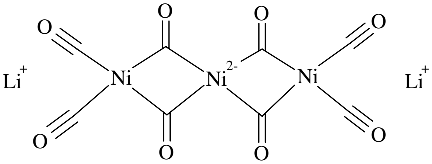
It may explode with water.

See Carbon: Alkali metals

See other METAL NON-METALLIDES

3102. Lithium octacarbonyltrinickelate
(Dilithium di-μ-carbonylhexacarbonlytrinickelate(2-))

[81181-45-5] (ion) **$C_8Li_2Ni_3O_8$**



Bailar, 1973, Vol. 3, 1117

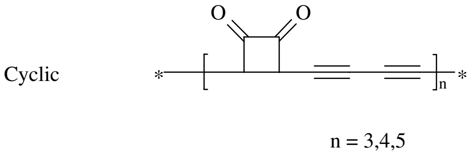
A pyrophoric salt.

See related CARBONYLMETALS

3103. Oligo(octacarbondioxide)

(Cyclo-*oligo*-butadiynyl-2,3-dioxocyclobutenylidene)

[123002-86-8] n = 3; [123002-87-9] n = 4; [ ] n=5 **$(C_8O_2)_n$**



Diederich, F. *et al., J. Amer. Chem. Soc.*, 1991, **113**(2), 495

These compounds exploded violently on heating above 85°C in an attempt to obtain melting points.

See 11,12-Diethynyl-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene

See other ACETYLENIC COMPOUNDS

3104. Rubidium graphite

[12193-29-2] **C_8Rb**

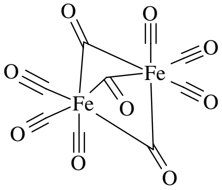
RbC_8

See Carbon: Alkali metals

See other METAL NON-METALLIDES

3105. Nonacarbonyldiiron

[20982-74-5] **$C_9Fe_2O_9$**



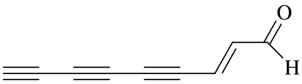
Anon., *ABCM Quart. Safety Summ.*, 1943, **14**, 18

Commercial iron carbonyl (fl.p.35°C) has an autoignition temperature in contact with brass of 93°C, lower than that of carbon disulfide.

See other CARBONYLMETALS

3106. 2-Nonen-4,6,8-triyn-1-al

[90271-76-4] **C_9H_4O**



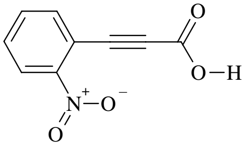
Bohlman, F. *et al., Chem. Ber.*, 1963, **96**, 2586

Extremely unstable, explodes after a few minutes at ambient temperature and ignites at 110°C.

See other ACETYLENIC COMPOUNDS

3107. 2-Nitrophenylpropiolic acid

[530-85-8] **$C_9H_5NO_4$**



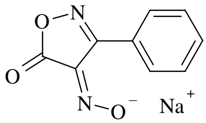
Sorbe, 1968, 152

It explodes above 150°C.

See other ACETYLENIC COMPOUNDS, NITROARYL COMPOUNDS, ORGANIC ACIDS

3108a. Sodium 3-phenylisoxazolin-4,5-dione-4-oximate

[70247-49-3] **$C_9H_5N_3NNaO_3$**



Wentrup, C. *et al., Angew. Chem. (Intern. Ed.)*, 1979, **18**, 467

It explodes on rapid heating, like the 5-methyl analogue and the silver salt.

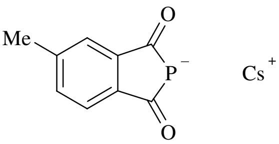
See Fulminic acid(reference 2)

See other N—O COMPOUNDS

See related OXIMES

3108b. Caesium 5-methylphthaloylphosphide (5-Methylisophosphoindoline-1,3-dione (1-) caesium(1+) salt) (Cesium 1*H*-isophosphindole-1,3(2H)dionide)

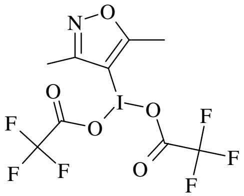
[342431-56-5] **$C_9H_6CsO_2P$**



Nelson, R. C. *et al., Organometallics*, 2001, **20**(8), 1705

On two occasions samples of this, or of a closely related phthaloylphosphide, spontaneously ignited in air. There is some possibility that small particles of caesium metal might have been present as an impurity.

3109. 3,5-Dimethyl-4-[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole
[57508-69-7] **$C_9H_6F_6INO_5$**



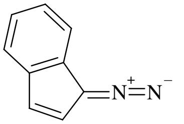
Preparative hazard

See [*I,I*-Bis(trifluoroacetoxy)iodo]benzene

See Peroxytrifluoroacetic acid: 4-Iodo-3,5-dimethylisoxazole

See other IODINE COMPOUNDS

3110. 1-Diazoindene
[35847-40-6] **$C_9H_6N_2$**



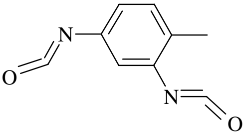
Quinn, S. *et al., Inorg. Chim. Acta*, 1981, **50**, 141—146

The preparation of this is hazardous, and it is recommended that diazoindene always be kept in solution.

See 4-Toluenesulfonyl azide

See other DIAZO COMPOUNDS

3111. 2,4-Diisocyanatotoluene
[584-84-9] **$C_9H_6N_2O_2$**



(*MCA SD-73*, 1971); *NSC 489*, 1977; *FPA H5*, 1972; *HCS 1980*, 907

Acyl chlorides, or Bases

MCA SD-73, 1971

The diisocyanate may undergo exothermic polymerisation in contact with bases or more than traces of acyl chlorides, sometimes used as stabilisers.

Manufacturing hazard

U.S. National Transportation Safety Board, Hazardous Materials Accident Report 7329, 2001

A rail tanker of wastes (exact origin unstated but perhaps distillation residues) sat five years before it was sent to a cement plant for incineration as fuel for the kilns. After sitting another three months there, it was found more viscous than usual and warmed to 90°C. At this point the tank started to pressurise, but seems to have cooled. Although samples were fluid, the bulk still proved too viscous to unload. Two days of further attempts followed, including rewarming to 80°C. A day later still, the tanker exploded into a fireball, the tank being thrown some 200 m. Analysis prior to the start of pressurisation had shown no water present. It is probable that localised overheating initiated polymerisation, blocking vents and bursting the tank.

Other reactants

Yoshida, 1980, 259

MRH values calculated for 13 combinations with oxidants are given.

Water

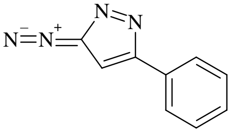
Kirk-Othmer, 1981, Vol. 13, 812

Polythene containers holding the diisocyanate may harden and burst in prolonged storage, because of slow absorption of water vapour through the wall leading to urea deposition from hydrolysis and generation of pressure of liberated carbon dioxide.

See other ORGANIC ISOCYANATES

3112. 3-Diazo-5-phenyl-3*H*-pyrazole

[62072-18-8] **$C_9H_6N_4$**



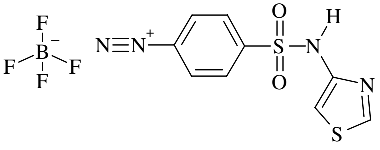
The light-sensitive crystalline solid is shock-sensitive and explodes at 115°C.

See entry DIAZOAZOLES

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS

3113. 5-(4-Diazoniobenzenesulfonamido)thiazole tetrafluoroborate

[41334-40-1] (ion) **$C_9H_7BF_4N_4O_2S$**



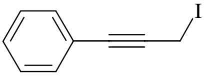
Zuber, F. *et al., Helv. Chim. Acta*, 1950, **33**, 1269—1271

It explodes at 135—137°C.

See entry DIAZONIUM TETRAHALOBORATES

3114. 3-Iodo-1-phenylpropyne

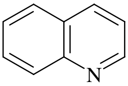
[73513-15-2] **C_9H_7I**



Whiting, M. C., *Chem. Eng. News*, 1972, **50**(23), 86
It detonated on distillation at around 180°C.
See other HALOACETYLENE DERIVATIVES

3115. Quinoline

[91-22-5] **C_9H_7N**



HCS 1980, 805

1. Blumann, A., *Proc. R. Aust. Chem. Inst.*, 1964, **31**, 286
2. *MCA Case History No. 1008*

The traditional unpredictably violent nature of the Skraup reaction (preparation of quinoline and derivatives by treating anilines with glycerol, sulfuric acid and an oxidant, usually nitrobenzene) is attributed to lack of stirring and adequate temperature control in many published descriptions [1]. A reaction on 450 l scale, in which sulfuric acid was added to a stirred mixture of aniline, glycerol, nitrobenzene, ferrous sulfate and water, went out of control soon after the addition. A 150 mm rupture disk blew out first, followed by the manhole cover of the vessel. The violent reaction was attributed to doubling the scale of the reaction, an unusually high ambient temperature (reaction contents at 32°C) and the accidental addition of excess acid. Experiment showed that a critical temperature of 120°C was attained immediately on addition of excess acid under these conditions [2].

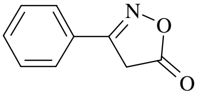
Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Heterocyclic bases

Hydrogen peroxide
See Hydrogen peroxide: Organic compounds (reference 2)

Linseed oil, Thionyl chloride
See Sulfinyl chloride: Linseed oil, etc.

Maleic anhydride
See Maleic anhydride: Bases, etc.
See other ORGANIC BASES

3116a. 3-Phenyl-5-isoxazolone
[7713-79-3] **$C_9H_7NO_2$**

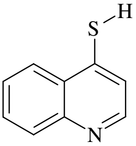


Sealed samples decompose exothermally above 105°C.

See entry ISOXAZOLES

See other N—O COMPOUNDS

3116b. 3-Quinolinethiol (3-Mercaptoquinoline)
[76076-35-2] **C_9H_7NS**



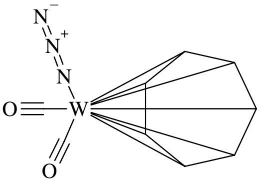
Preparative Hazard

Laquidara, J., *Chem. Eng. News*, 2001, **79**(28), 6

A preparation of quinoline-3-thiol from the diazonium salt, according to prior literature, and using potassium ethyl xanthate, abnormally threw down a solid during extraction of the product into ether. This solid, filtered and dried, exploded on prodding with a metal spatula. The solid had an nmr spectrum consistent with the expected product, an *S*-aryl-*O*-ethyl xanthate. Although the author appears aware of only the arenediazosulfide hazard, this must have been the *S*-arenediazoxanthate. A misprint renders quinoline as quinine.

See other DIAZONIUM SULFIDES AND DERIVATIVES

3117. Dicarbonyl-π-cycloheptatrienyltungsten azide
[59589-13-8] **$C_9H_7N_3O_2W$**

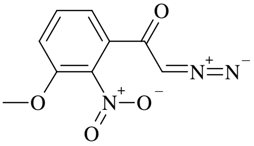


Hoch, G. *et al., Z. Naturforsch. B*, 1976, **31B**, 295

It was insensitive to shock, but decomposed explosively at 130°C.

See related CARBONYLMETALS, METAL AZIDES, ORGANOMETALLICS

3118. 3-Methoxy-2-nitrobenzoyldiazomethane
[24115-83-1] **$C_9H_7N_3O_4$**



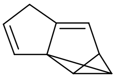
Alone, or Sulfuric acid

Musajo, L. *et al., Gazz. Chim. Ital.*, 1950, **80**, 171—176

The diazoketone explodes at 138—140°C, or on treatment with conc. sulfuric acid.

See other DIAZO COMPOUNDS, NITROARYL COMPOUNDS

3119. Tetracyclo[4.3.$0^{3,5}$.$0^{4,6}$]nona-1,7-diene (2,4-Dihydro-1*H*-1,2,6*a*-methanopentalene)
[85861-34-3] **C_9H_8**

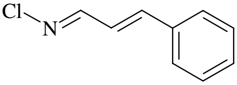


Burger, U. *et al., Helv. Chim. Acta*, 1983, **66**, 60—67

The highly strained hydrocarbon, produced from dilithiopentalene and chlorocarbene, explodes violently at temperatures as low as —40°C when concentrated. Other isomers are probably similar.

See other DIENES, STRAINED-RING COMPOUNDS

3120. *N*-Chlorocinnamaldimine (3-Chlorimino-1-phenylpropene)
[ ] **C_9H_8ClN**



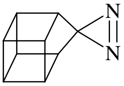
Hauser, C. R. *et al., J. Amer. Chem. Soc.*, 1935, **57**, 570

It decomposes vigorously after storage at ambient temperature for 30 m.

See other N-HALOGEN COMPOUNDS

See related DIENES

3121. Spiro(homocubane-9,9′-diazirine) (Spiro[3*H*-diazirine-3,9′-pentacyclo[4,3,0,0,^{2,5}0,^{3,8}0,^{4,7}]nonane])
[129215-84-5] **$C_9H_8N_2$**



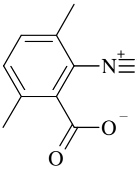
Platz, M. S. *et al., J. Amer. Chem. Soc.*, 1991, **113**, 4991

A white, dangerously explosive solid, apparently storable at room temperature but decomposing before melting.

See other DIAZIRINES, STRAINED-RING COMPOUNDS

3122. 3,5-Dimethylbenzenediazonium-2-carboxylate

[68596-88-3] **$C_9H_8N_2O_2$**



Wilcox, C. F. *et al., J. Amer. Chem. Soc.*, 1984, **106**, 7196

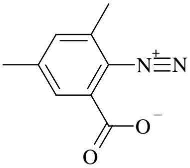
It is more sensitive to thermal decomposition than other diazonium carboxylates, and will decompose readily when inadequate stirring, large scale or excessively rapid diazotisation produces too large a temperature rise. There is significant potential for violent eruption of suspensions, or detonation of the filtered solid, and all recommended precautions should be used.

See 2-Carboxy-3,6-dimethylbenzenediazonium chloride

See other DIAZONIUM CARBOXYLATES

3123. 4,6-Dimethylbenzenediazonium-2-carboxylate

[ ] **$C_9H_8N_2O_2$**



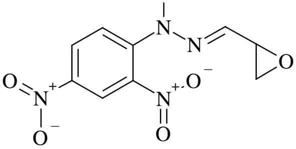
Gommper, R. *et al., Chem. Ber.*, 1968, **101**, 2348

It is a highly explosive solid.

See other DIAZONIUM CARBOXYLATES

3124. 2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone

[ ] **$C_9H_8N_4O_5$**



Payne, G. B., *J. Amer. Chem. Soc.*, 1959, **81**, 4903

Although it melts at 96—98°C in a capillary, 0.5 g in a test tube decomposed explosively at 100°C.

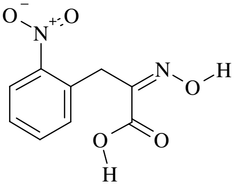
See 2,3-Epoxypropionaldehyde oxime

See other 1,2-EPOXIDES, POLYNITROARYL COMPOUNDS

See related HYDRAZONES

3125. 3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid (*o*-Nitrophenylpyruvic acid oxime)

[27878-36-0] **$C_9H_8N_2O_5$**



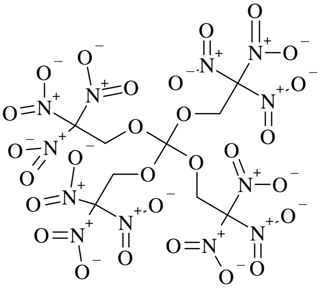
CHETAH ,1990, 187

Shock sensitive

See other NITROARYL COMPOUNDS, ORGANIC ACIDS, OXIMES

3126. Tetrakis(2,2,2-trinitroethyl)orthocarbonate

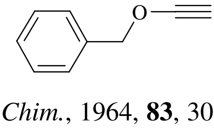
[14548-58-4] **$C_9H_8N_{12}O_{28}$**



See entry TRINITROETHYL ORTHOESTERS

3127. Benzyloxyacetylene

[40089-12-1] **C_9H_8O**



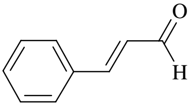
Olsman, H. *et al., Rec. Trav. Chim.*, 1964, **83**, 305

If heated above 60°C during vacuum distillation, explosive rearrangement occurs.

See other ACETYLENIC COMPOUNDS, BENZYL COMPOUNDS

3128. Cinnamaldehyde (3-Phenylpropenal)

[104-55-2] **C_9H_8O**



HCS 1980, 316

Sodium hydroxide

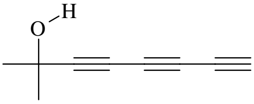
Morrell, S. H., private comm., 1968

Rags soaked in sodium hydroxide and in the aldehyde overheated and ignited owing to aerobic oxidation when they came into contact in a waste bin.

See other ALDEHYDES, PEROXIDISABLE COMPOUNDS, SELF-HEATING AND IGNITION INCIDENTS

3129. 2-Methyl-3,5,7-octatriyn-2-ol

[ ] **C_9H_8O**



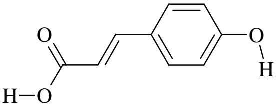
Cook, C. J. *et al., J. Chem. Soc.*, 1952, 2885, 2890

The crude material invariably deflagrated at ambient temperature, and once during drying at 0°C/0.013 mbar.

See other ACETYLENIC COMPOUNDS

3130. 4-Hydroxy-*trans*-cinnamic acid

[7400-08-0] **$C_9H_8O_3$**



Tanaka, Y. *et al., Proc. 4th Int. Conf. High Press. (1974)*, 704, 1975

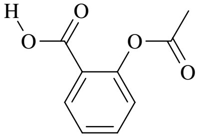
During spontaneous solid-state polymerisation at 325°C/8—10 kbar, the acid exploded violently.

See HIGH PRESSURE REACTION TECHNIQUES

See other ORGANIC ACIDS, POLYMERISATION INCIDENTS

3131. *O*-Acetylsalicylic acid

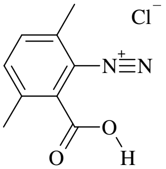
[50-78-2] **$C_9H_8O_4$**



For experimental investigation of aspirin powder explosions,
See entry DUST EXPLOSION INCIDENTS (reference 18)
See other ORGANIC ACIDS

3132a. 2-Carboxy-3,6-dimethylbenzenediazonium chloride

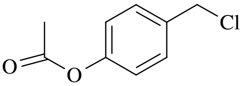
[36794-93-1] **$C_9H_9ClN_2O_2$**



Hart, H. *et al., J. Org. Chem.*, 1972, **37**, 4272
The compound (the hydrochloride of the internal carboxylate salt) appears to be stable for considerable periods at ambient temperature, but explodes on melting at 88°C.
See other ORGANIC ACIDS
See related DIAZONIUM CARBOXYLATES

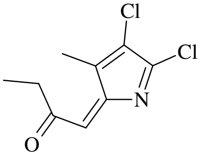
3132b. 4-Acetoxybenzyl chloride (4-Chloromethylphenyl acetate) ((4-Acetoxyphenyl)methyl chloride)

[39720-27-9] **$C_9H_9ClO_2$**



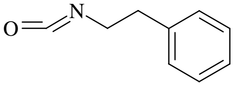
Anon., personal communication, 1999
A 5g sample, from which a few drops had been taken, was stored for four years. It was then observed to have become viscous and was set aside for disposal. Within three days it blew off the cap of its bottle, and that of a plastic secondary container. The contents had become a solid foam. Trace contamination cannot be absolutely excluded, but this looks like an autocatalytic Friedel Crafts polymerisation of a benzyl halide. It would represent serious danger on a larger scale.
See other BENZYL COMPOUNDS

3132c. 1-(4,5-Dichloro-3-methyl-2*H*-pyrrol-2-ylidene)-2-butanone
[199917-28-7] **$C_9H_9Cl_2NO$**



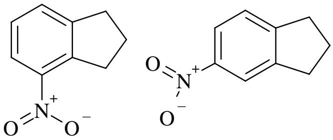
Baird, M. S. *et al., Tetrahedron Lett.*, 1997, **38**(47), 8271
This compound was found to be unstable, decomposing vigorously in the absence of solvent.

3133. 2-Phenylethyl isocyanate
[14649-03-7] **C_9H_9NO**



Energy of decomposition (in range 220—350°C) measured as 0.50 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ORGANIC ISOCYANATES

3134. *mixo*-Nitroindane
[34701-14-9 , 7436-07-9] (4- and 5- isomers, resp.) **$C_9H_9NO_2$**

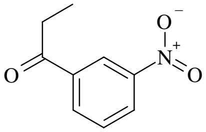


1. Lindner, J. *et al., Ber.*, 1927, **60**, 435
2. Gribble, G. W., *Chem. Eng. News*, 1973, **51**(6), 30, 39

The crude mixture of 4- and 5-nitroindanes produced by mixed acid nitration of indane following a literature method [1] is hazardous to purify by distillation. The warm residue from distillation of 15 mmol at 80°C/1.3 mbar exploded on admission of air, and a 1.3 mol batch exploded as distillation began under the same conditions. Removal of higher-boiling poly-nitrated material before distillation is recommended.
See other NITROARYL COMPOUNDS

3135. 3-Nitropropiophenone

[17408-16-1] **$C_9H_9NO_3$**



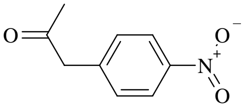
Preparative hazard

See Nitric acid: Propiophenone, etc.

See other NITROARYL COMPOUNDS

3136. 4-Nitrophenylpropan-2-one

[5332-96-7] **$C_9H_9NO_3$**



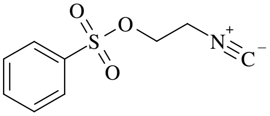
Preparative Hazard

See 4-Nitrophenylacetic acid

See other NITROARYL COMPOUNDS

3137. 2-Isocyanoethyl benzenesulfonate

[57678-14-5] **$C_9H_9NO_3S$**



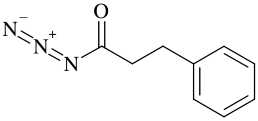
Matteson, D. S. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 3761

Heating the product under vacuum to remove pyridine solvent caused a moderately forceful explosion.

See other ORGANIC ISOCYANATES, SULFUR ESTERS

3138. 3-Phenylpropionyl azide

[ ] **$C_9H_9N_3O$**



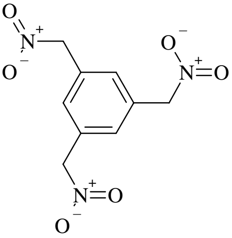
Curtiss, T. *et al., J. Prakt. Chem.*, 1901, **64**, 297

A sample exploded on a hot water bath.

See other ACYL AZIDES

3139. 1,3,5-Tris(nitromethyl)benzene

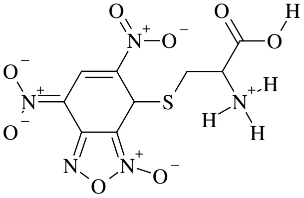
[ ] $C_9H_9N_3O_6$



See Nitric acid: Hydrocarbons (reference 8)
See related POLYNITROALKYL COMPOUNDS, POLYNITROARYL COMPOUNDS

3140. 4-(2-Ammonio-2-carboxyethylthio)-5,7-dinitro-4,5-dihydrobenzofurazanide *N*-oxide (4,6-Dinitrobenzofurazan *N*-oxide . cysteine complex)

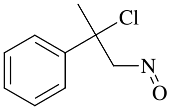
[79263-47-1] $C_9H_9N_5O_8S$



Strauss, M. J. *et al., Tetrahedron Lett.*, 1981, **22**, 1945—1948
When thoroughly dry, the cysteine complex of 5,7-dinitrobenzofurazan *N*-oxide exploded on heating.
See other FURAZAN N-OXIDES

3141. 2-Chloro-1-nitroso-2-phenylpropane

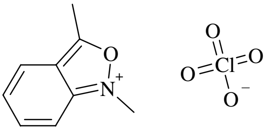
[6866-10-0] $C_9H_{10}ClNO$



MCA Case History No. 747

A sample of the air-dried material (which is probably the dimer) decomposed vigorously on keeping in a closed bottle at ambient temperature overnight.
See other NITROSO COMPOUNDS

3142a. 1,3-Dimethyl-2,1-benzisoxazolium perchlorate
[63609-41-6] **$C_9H_{10}ClNO_5$**

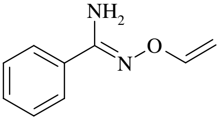


Haley, N. F., *J. Org. Chem.*, 1978, **43**, 1236

The salt, m.p. 152°, explodes at 154°C.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

3142b. *N*-Ethenyloxybenzenecarboximidamide
[263699-24-7] **$C_9H_{10}N_2O$**

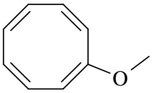


Trofimov, B. A. *et al., Synthesis*, 2001, (16), 2427

This compound is reported as decomposing explosively at around 150°C.

See other N—O COMPOUNDS

3143. Methoxy-1,3,5,7-cyclooctatetraene
[7176-89-8] **$C_9H_{10}O$**



Oxygen

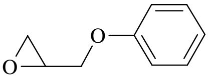
Adam, W. *et al., Tetrahedron Lett.*, 1982, **23**, 2837—2840

The evaporated residue from sensitised photochemical oxidation of the polyene ignited spontaneously, on several occasions explosions occurring.

See other PEROXIDISABLE COMPOUNDS, SELF-HEATING AND IGNITION INCIDENTS

See related DIENES

3144. 3-Phenoxy-1,2-epoxypropane (Glycidyl phenyl ether)
[122-60-1] **$C_9H_{10}O$**

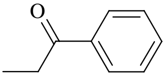


Energy of decomposition (in range 360—450°C) measured as 0.626 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

3145. Propiophenone

[93-55-0] **$C_9H_{10}O$**

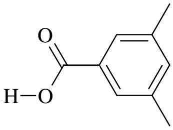


Nitric acid, Sulfuric acid

See Nitric acid: Propiophenone, etc.

3146. 3,5-Dimethylbenzoic acid

[499-06-9] **$C_9H_{10}O_2$**



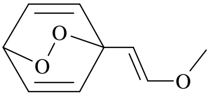
Preparative hazard

See Nitric acid: Hydrocarbons (reference 8)

See other ORGANIC ACIDS

3147. 1-(*cis*-Methoxyvinyl)-1,4-endoperoxy-2,5-cyclohexadiene (*Z*-1-(2-Methoxyethenyl)-2,3-dioxabicyclo[2.2.2]octa-5,7-diene)

[ ] **$C_9H_{10}O_3$**



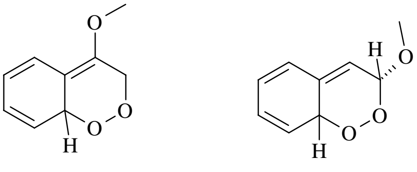
Matsumoto, M. *et al., Tetrahedron. Lett.*, 1979, 1607—1610

The product of sensitised photooxidation of *cis*-2-methoxystyrene is explosive.

See other CYCLIC PEROXIDES

3148. 3- or 4-Methoxy-5,6-benzo-6*H*-1,2-dioxin

[69681-97-6, 69681-98-7, resp.] **$C_9H_{10}O_3$**



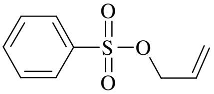
Lerdal, D. *et al., Tetrahedron. Lett.*, 1978, 3227—3228

Both isomers decomposed violently on warming in absence of solvent.

See other CYCLIC PEROXIDES

3149. Allyl benzenesulfonate

[7575-57-7] **$C_9H_{10}O_3S$**



Dye, W. T. *et al., Chem. Eng. News*, 1950, **28**, 3452

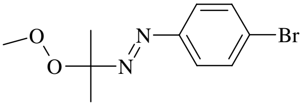
The residue from vacuum distillation at 92—135°C/2.6 mbar darkened, thickened, then exploded after removal of the heat source.

For precautions, *see* Triallyl phosphate

See other ALLYL COMPOUNDS, SULFUR ESTERS

3150. 2-(4-Bromophenylazo)-2-propyl hydroperoxide

[72447-41-7] **$C_9H_{11}BrN_2O_2$**

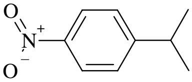


See entry α-PHENYLAZO HYDROPEROXIDES (reference 4)

See related ALKYL HYDROPEROXIDES, AZO COMPOUNDS

3151. 4-Nitroisopropylbenzene

[1817-47-6] **$C_9H_{11}NO_2$**



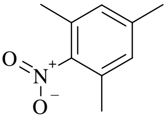
High rate of pressure increase during exothermal decomposition.

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

See other NITROARYL COMPOUNDS

3152. Nitromesitylene

[603-71-4] **$C_9H_{11}NO_2$**



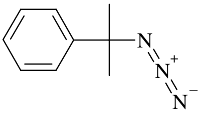
Preparative hazard

See Nitric acid: Hydrocarbons (references 7,8)

See other NITROARYL COMPOUNDS

3154. 2-Azido-2-phenylpropane

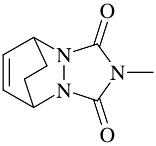
[32366-26-0] **$C_9H_{11}N_3$**



Energy of exothermic decomposition in range 180—270°C was measured as 1.2 kJ/g
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ORGANIC AZIDES

3155. 4-Methyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undeca-8-ene-3,5-dione (5,8-Dihydro-2-methyl-5,8-ethano-1*H*-[1,2,4]triazolo[1,2*a*] pyridazine-1,3(2*H*)dione)

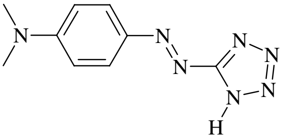
[78790-57-5] **$C_9H_{11}N_3O_2$**



Hydrogen peroxide, Potassium hydroxide
See Hydrogen peroxide: 4-Methyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undeca-8-ene-3,5-dione

3156. 5-(4-Dimethylaminobenzeneazo)tetrazole

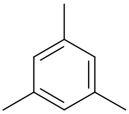
[53004-03-8] **$C_9H_{11}N_7$**



Thiele, J., *Ann.*, 1892, **270**, 61
It explodes at 155°C.
See other AZO COMPOUNDS, TETRAZOLES

3157a. Mesitylene (1,3,5-Trimethylbenzene)

[108-67-8] **C_9H_{12}**



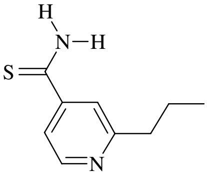
HCS 1980, 621

Nitric acid

See Nitric acid: Hydrocarbons (reference 8)

3157b. 2-Propylpyridine-4-carbothioamide (2-Propyl(thioisonicotinamide))

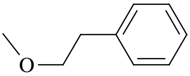
[14222-60-7] **$C_9H_{12}N_2S$**



See FRICTIONAL INITIATION INCIDENTS (reference 2)

3158. 2-Methoxyethylbenzene

[3558-60-9] **$C_9H_{12}O$**

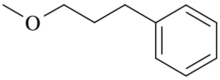


Nitric acid

See Nitric acid: 2-Methoxyethylbenzene, Sulfuric acid

3159. 3-Phenylpropanol

[122-97-4] **$C_9H_{12}O$**

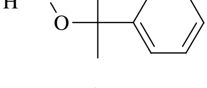


Phosphorus tribromide

See Phosphorus tribromide: 3-Phenylpropanol

3160. 2-Phenyl-2-propyl hydroperoxide (Cumyl hydroperoxide) (Cumene hydroperoxide)

[80-15-9] **$C_9H_{12}O_2$**



1. Leroux, A., *Mém. Poudres*, 1955, **37**, 49
2. Simon, A. H. *et al., Chem. Ber.*, 1957, **90**, 1024
3. Hulanicki, A., *Chem. Anal.* (Warsaw), 1973, **18**, 723—726
4. *MCA Case History No. 906*
5. Leleu, *Cahiers*, 1973, (71), 226
6. Fleming, J. B. *et al., Hydrocarbon Process.*, 1976, **55**(1), 185—196

7. Redoshkin, B. A. *et al., Chem. Abs.*, 1964, **60**, 14359h
8. Antonovskii, V. L. *et al., Chem. Abs.*, 1964, **60**, 14360c
9. Kletz, T. A., *Loss Prev.*, 1979, **12**, 98
10. Anon., *Loss Prev. Bull.*, 1986, (071), 9
11. Schwab, R. F., *Loss. Prev. Bull.*, 1988, (083), 20—32
12. Anon., *Loss Prev. Bull.*, 1992, **103**, 31
13. Francisco, M. A., *Chem. Eng. News*, 1993, **71**(22), 4
14. Shanley, E. S., *Chem. Eng. News*, 1993, **71**(35), 61
15. Wang, Y-H. *et al., Ind. Eng. Chem. Res.*, 2001, **40**(4), 1125
16. Kozak, G. D. *et al., Chem. Abs.*, 2004, **141**, 9242t

The explosibility of this unusually stable hydroperoxide has been investigated [1]. It is difficult, but not impossible, to induce explosive decomposition [2]. A colorimetric method of analysing mixtures of cumene and its hydroperoxide which involves alkaline decomposition of the latter is safer than the use of acidic conditions, or of reducants, which may cause explosive reactions [3]. During vacuum concentration of the hydroperoxide by evaporation of cumene, a 6.5m^3 quantity of the 36% material decomposed explosively after storage at 109°C for 5 h. Catalytic decomposition under near-adiabatic conditions may have been involved [4]. At the end of concentration from hexane, after purification, 100 ml of peroxide exploded violently for no apparent reason; isolation of no more than 5g is recommended [13]. Contact with copper, copper or lead alloys, mineral acids or reducants may lead to violent decomposition [5]. Cobalt also catalyses the decomposition reaction which is autocatalytic. The acid cleavage reaction used industrially is highly exothermic, and safety aspects of commercial phenol/acetone processes are discussed fully [6]. Much detailed kinetic work has also been published [7,8]. Five explosions due to overheating and subsequent decomposition of the concentrated solutions in cumene have been noted. Another explosion arose from reduced flow of acid gas used in the cleavage reaction because the cylinder was outdoors on a cold night. The reduced flow led to spurious control signals which eventually caused the explosion [9]. During a shut-down, a 100 t quantity of hydroperoxide solution in intermediate storage was being kept hot with steam but became overheated, causing cumene to vent. The vapour ignited explosively and ruptured the storage tank [10]. A detailed analysis of the incident is available [11]. A drum of the hydroperoxide exploded, this was attributed to possible contamination with sodium hydroxymethylsulfonate. This might form catalytic acids if oxidised, but the drum had been sampled with a, possibly corroded, stainless steel dip pipe [12]. Calorimetric study of cumene hydroperoxide showed its decomposition accelerated by acid, alkali and iron(III) compounds, especially the chloride. The last two changed the product spectrum. Ferric sulfate and oxide were far less effective than the chloride [probably poor miscibility – Ed.], which showed exothermic decomposition from 40°C. Alkali, from 60°C, was reckoned the most dangerous contaminant [15].

CHETAH calculations for energy/hazard of an hypothetical decomposition reaction to carbon, water and methane are reported [14]. An experimental study of deflagration and detonation aimed at understanding the chemical mechanisms has been reported [16].

See COMPUTATION OF REACTIVE CHEMICAL HAZARDS, THERMAL EXPLOSIONS
See other CATALYTIC IMPURITY INCIDENTS, CORROSION INCIDENTS

Charcoal

Leleu, *Cahiers*, 1980, (99), 278

Contact with charcoal powder at ambient temperature gives a strong exotherm (probably owing to traces of heavy metals present).

1,2-Dibromo-1,2-diisocyanatoethane polymers

Lapshin, N. M. *et al., Chem. Abs.*, 1974, **81**, 64013

A mixture of the dimeric and trimeric dibromo compounds with the hydroperoxide in benzene may react vigorously or explode if the solution is heated to concentrate it.

Iodides

Duswalt A. A., *Chem. Eng. News*, 1990, **68**(6), 2

Following a laboratory incident, cumene hydroperoxide was shown to be explosively decomposed by catalytic sodium iodide.

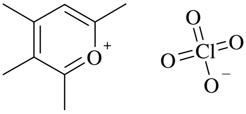
Other reactants

Yoshida, 1980, 105

MRH values calculated for 15 combinations with oxidisable materials are given.

See other ALKYL HYDROPEROXIDES, COMMERCIAL ORGANIC PEROXIDES

3161. 2,3,4,6-Tetramethylpyrilium perchlorate
[35941-38-9] **$C_9H_{13}ClO_5$**

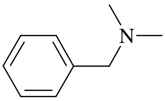


Balaban, A. T. *et al., Org. Prep. Proced. Int.*, 1982, **14**, 31—38

It must be handled cautiously.

See other NON-METAL PERCHLORATES

3162. Benzyldimethylamine
[28262-13-7] **$C_9H_{13}N$**

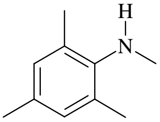


Cellulose nitrate

See CELLULOSE NITRATE: Amines

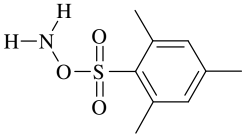
See other BENZYL COMPOUNDS, ORGANIC BASES

3163. 2,4,6-Trimethylaniline
[88-05-1] **$C_9H_{13}N$**



Nitrosyl perchlorate
See Nitrosyl perchlorate: Organic materials

3164. *O*-Mesitylenesulfonylhydroxylamine
[36016-40-7] **$C_9H_{13}NO_3S$**



1. Tamura, Y. *et al., Tetrahedron Lett.*, 1972, **40**, 4133
2. Ning, R. Y., *Chem. Eng. News*, 1973, **51**(51), 36—37
3. Carpino, L. A., *J. Amer. Chem. Soc.*, 1960, **82**, 3134
4. Ning, R. Y., private comm., 1974
5. Johnson, C. R. *et al., J. Org. Chem.*, **39**, 2459, footnote 15
6. Scopes, D. I. C. *et al., J. Org. Chem.*, 1977, **42**, 376
7. Dillard, R. D. *et al., J. Med. Chem.*, 1980, **23**, 718
8. Fluka advertisement, *J. Org. Chem.*, 1980, **45**(9), cover ii

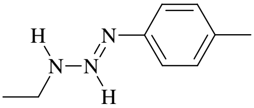
The title compound was prepared following a published procedure [1] and a dried sample decomposed soon after putting it into an amber bottle for storage, the screw cap being shattered [2]. Although the instability of the compound had been mentioned [3], no suggestion of violent decomposition had previously been made. It seems likely that traces of surface alkali in the soda-glass bottle had catalysed both the formation of the highly active imidogen radical ($HN^{\cdot}$) from the base-labile compound, and its subsequent exothermic decomposition. Storage in dichloromethane solution appears safe [4]. The small crystals produced by a modified method appear to be safe in storage at 0°C, or in use [5]. Attempted vacuum drying of the compound at ambient temperature led to a mild explosion. Subsequently, a solution of the wet solid in dimethoxyethane was dried over molecular sieve and used in further work [6]. The solid may explode violently when heated to 60°C. Large amounts should be used either in solution or as the crystalline solid. The neat molten liquid form should be avoided, as it evolves heat on crystallisation. It is best to avoid storage and generate the reagent as needed [7]. A stable precursor, *tert*-butyl *N*-mesitylenesulfonyloxycarbamate has become available [8].

See O-4-Toluenesulfonylhydroxylamine

See other CATALYTIC IMPURITY INCIDENTS, GLASS INCIDENTS, N—O COMPOUNDS

3165. 3-Ethyl-1(4-methylphenyl)triazene

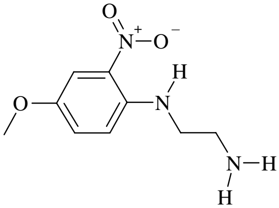
[50707-40-9] **$C_9H_{13}N_3$**



Anon., *Loss Prev. Bull.*, 1980, (030), 160
A 5 g sample was distilled under vacuum uneventfully from a bulb tube with air-bath heating, but a 50 g portion exploded violently when distilled at 0.13 mbar from an oil-bath at 120°C.
See other TRIAZENES

3166. 2-(2-Aminoethylamino)-5-methoxynitrobenzene

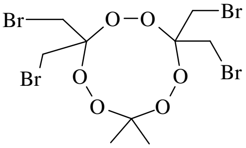
[13556-31-5] **$C_9H_{13}N_3O_3$**



See N-(2-Nitrophenyl)-1,2-diaminoethane
See other NITROARYL COMPOUNDS

3167. 3,3,6,6-Tetrakis(bromomethyl)-9,9-dimethyl-1,2,4,5,7,8-hexoxonane

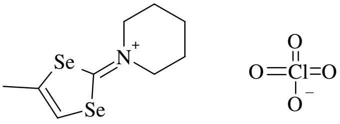
[16007-16-2] **$C_9H_{14}Br_4O_6$**



Schulz, M. *et al., Chem. Ber.*, 1967, **100**, 2245
It explodes on impact or friction, as do the tetrachloro- and 9-ethyl-9-methyl analogues.
See other CYCLIC PEROXIDES

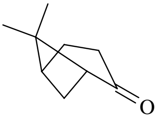
3168. 1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate

[53808-72-3] **$C_9H_{14}ClNO_4Se_2$**



See entry 1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES
See other PERCHLORATE SALTS OF NITROGENOUS BASES

3169. 6,6-Dimethylbicyclo[3.1.1]heptan-2-one (Nopinone)
[24903-95-5] [77982-63-9] S- isomer **$C_9H_{14}O$**



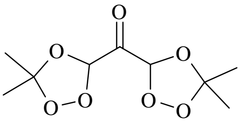
Preparative hazard

1. Gordon, P. M., *Chem. Eng. News*, 1990, **68**(30), 2
2. Ferreira, J. T. B., *ibid.*, (50), 2
3. Weissman, S., *ibid.*, 1991, **69**(4), 2

Several reports have been received of explosion during work-up of the products obtained from ozonolysis of pinene, despite prior treatment with reducants. A safe alternative procedure is given in [3].

See OZONIDES

3170. 2,6-Dimethyl-2,5-heptadien-4-one diozonide
[ ] **$C_9H_{14}O_7$**

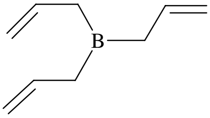


Harries, G. *et al., Ann.*, 1910, **374**, 338

'Phorone' diozonide ignites on warming to ambient temperature.

See other OZONIDES

3171. Tri-2-propenylborane (Triallylborane)
[688-61-9] **$C_9H_{15}B$**



Borane

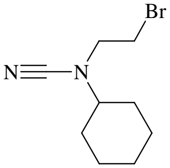
Alder, R. W. *et al., J. Chem. Soc., Perk. I*, 1996, (7), 657

The 1:1 adduct is highly pyrophoric, so too is its pyrolysis product. Both are polymeric, diborabicycloundecane is not.

See other ALKYLBORANES

3172. *N*-Cyano-2-bromoethylcyclohexylamine

[53182-16-4] **$C_9H_{15}BrN_2$**



Anon., *BCISC Quart. Safety Summ.*, 1964, **35**, 23

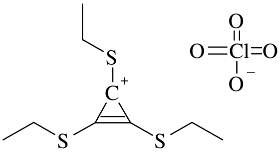
The reaction product from *N*-cyclohexylaziridine and cyanogen bromide (believed to be the title compound) exploded violently on attempted distillation at 160°C/0.5 mbar.

See N-Cyano-2-bromoethylbutylamine

See other CYANO COMPOUNDS

3173. Tris(ethylthio)cyclopropenium perchlorate

[50744-08-6] **$C_9H_{15}ClO_4S_3$**



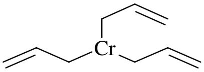
Sunderlin, K. G. R., *Chem. Eng. News*, 1974, **52**(31), 3

Some 50 g of the compound had been prepared by a method used for analogous compounds, and the solvent-free oil had been left to crystallise. Some hours later it exploded with considerable violence. Preparation of this and related compounds by other workers had been uneventful.

See other NON-METAL PERCHLORATES

3174. Triallylchromium

[12082-46-1] **$C_9H_{15}Cr$**



O’Brien, S. *et al., Inorg. Chem.*, 1972, **13**, 79

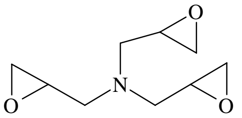
Triallylchromium and its thermal decomposition products are pyrophoric in air.

See other ALLYL COMPOUNDS

See related ALKYLMETALS

3175. Nitrilotris(oxiranemethane) (Triglycidylamine)

[61014-23-1] **$C_9H_{15}NO_3$**



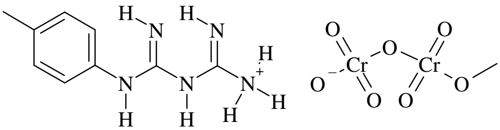
McKelvey, J. *et al., J. Org. Chem.*, 1960, **25**, 1424

The crude product polymerises violently during vacuum distillation. The pure is storable cool

See other 1,2-EPOXIDES

3176. 4-Tolylbiguanidium hydrogen dichromate

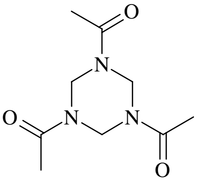
[15760-46-0] **$C_9H_{15}Cr_2N_5O_7$**



See entry DICHROMATE SALTS OF NITROGENOUS BASES

3177. 1,3,5-Triacetylhexahydro-1,3,5-triazine

[26028-46-6] **$C_9H_{15}N_3O_3$**

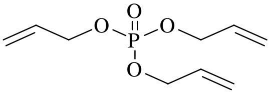


Nitric acid, Trifluoroacetic anhydride

See Nitric acid: 1,3,5-Triacetylhexahydro-1,3,5-triazine, etc.

3178. Triallyl phosphate

[1623-19-4] **$C_9H_{15}O_4P$**



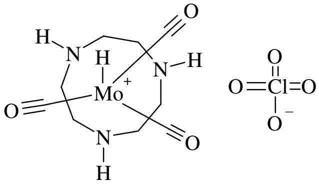
1. Dye, W. T. *et al., Chem. Eng. News*, 1950, **28**, 3452
2. Steinberg, G. M., *Chem. Eng. News*, 1950, **28**, 3755

Alkali-washed material, stabilised with 0.25% of pyrogallol, was distilled at 103°C/4 mbar until slight decomposition began. The heating mantle was then removed and the still-pot temperature had fallen below its maximum value of 135°C when the residue exploded violently [1]. The presence of solid alkali [2] or 5% of phenolic inhibitor is recommended, together with low-temperature high-vacuum distillation, to avoid formation of acidic decomposition products, which catalyse rapid exothermic polymerisation.

See other ALLYL COMPOUNDS, CATALYTIC IMPURITY INCIDENTS, PHOSPHORUS ESTERS

3179. 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate

[ ] **$C_9H_{16}ClMoN_3O_7$**

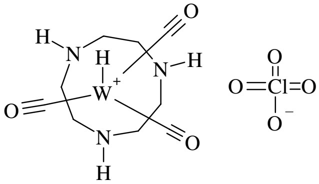


See 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, below

See related AMMINEMETAL OXOSALTS, CARBONYLMETALS

3180. 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate

[88253-43-4] **$C_9H_{16}ClN_3O_7W$**



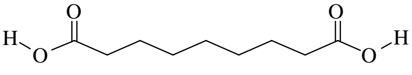
Chaudhuri, P. *et al., Inorg. Chem.*, 1984, **23**, 429

The dry tungsten and molybdenum complexes are extremely explosive when dry; handle no more than 10 mg portions. The corresponding Mo complexes with Br or I replacing H are also explosive.

See related AMMINEMETAL OXOSALTS, CARBONYLMETALS

3181. Azelaic acid

[123-99-9] **$C_9H_{16}O_4$**



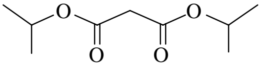
Hydrogen peroxide, Sulfuric acid

See Hydrogen peroxide: Azelaic acid, Sulfuric acid

See other ORGANIC ACIDS

3182. Diisopropyl malonate

[13195-64-7] **$C_9H_{16}O_4$**

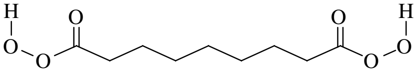


Sulfinyl chloride

See Sulfinyl chloride: Diisopropyl malonate

3183. Diperoxyazelaic acid

[1941-79-3] **$C_9H_{16}O_6$**



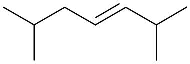
Preparative hazard

See Hydrogen peroxide: Azelaic acid, Sulfuric acid

See other PEROXYACIDS

†3184. 2,6-Dimethyl-3-heptene

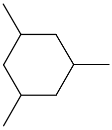
[2738-18-3] **C_9H_{18}**



See other ALKENES

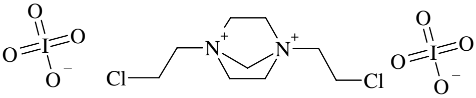
†3185. 1,3,5-Trimethylcyclohexane

[1795-27-3] **C_9H_{18}**



3186. 1,4-Bis(2-chloroethyl)-1,4-bis(azonia)bicyclo[2.2.1]heptane periodate

[77628-04-7] **$C_9H_{18}Cl_2I_2N_2O_8$**



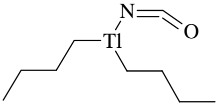
Pettit, G. R. *et al., Can. J. Chem.*, 1981, **59**, 218, 220

It exploded violently at about 150°C, or when ignited openly or on gentle impact.

See related PERCHLORATE SALTS OF NITROGENOUS BASES

3187. Dibutylthallium isocyanate

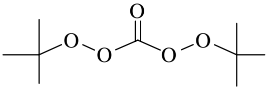
[74637-34-6] **$C_9H_{18}NOTl$**



Srinastava, T. N. *et al., Indian J. Chem. Sect. A*, 1980, **19A**, 480
It explodes at 35°C.
See other N-METAL DERIVATIVES
See related ALKYLMETALS, METAL CYANATES

3188. Di-*tert*-butyl diperoxycarbonate

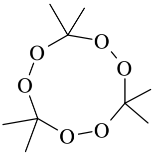
[3236-56-4] **$C_9H_{18}O_5$**



A partially decomposed sample exploded violently at 135°C.
See entry PEROXYCARBONATE ESTERS
See other PEROXYESTERS

3189. 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane

[17088-37-8] **$C_9H_{18}O_6$**

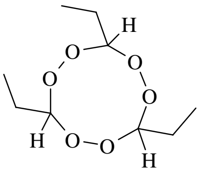


1. Dilthey, W. *et al., J. Prakt. Chem.*, 1940, **154**, 219
2. Rohrlich, M. *et al., Z. Ges. Schiess u. Sprengstoffw.*, 1943, **38**, 97—99
3. Lefebvre, M. H. *et al., Chem. Abs.* 2004, **141**, 176244b

This trimeric acetone peroxide is powerfully explosive [1], and will perforate a steel plate when heated on it [2]. Its properties as an explosive have been studied, it is too sensitive for safety [3].
See 6-Aminopenicillanic acid *S*-oxide
  Hydrogen peroxide: Ketones, Nitric acid
  Ozone: Citronellic acid
See other CYCLIC PEROXIDES

3190. 3,6,9-Triethyl-1,2,4,5,7,8-hexoxonane

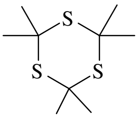
[ ] **$C_9H_{18}O_6$**



Rieche, A. *et al., Ber.*, 1939, **72**, 1938
This trimeric 'propylidene peroxide', formed from propanal and hydrogen peroxide, is an extremely explosive and friction-sensitive oil.
See other CYCLIC PEROXIDES

3191. 2,2,4,4,6,6-Hexamethyltrithiane

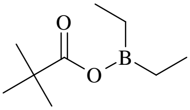
[828-26-2] **$C_9H_{18}S_3$**



Nitric acid
See Nitric acid: 2,2,4,4,6,6-Hexamethyltrithiane

3192. Pivaloyloxydiethylborane

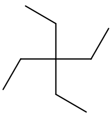
[32970-52-8] **$C_9H_{19}O_2$**



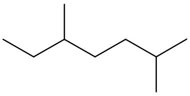
Air, or Water
Köster, R. *et al., Inorg. Synth.*, 1983, **22**, 196, 189
It reacts violently with air or water.
See related ACID ANHYDRIDES, ALKYLBORANES

†3193. 3,3-Diethylpentane

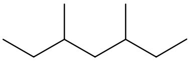
[1067-20-5] **C_9H_{20}**



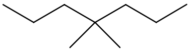
†3194. 2,5-Dimethylheptane
[2216-30-0] **C_9H_{20}**



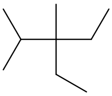
†3195. 3,5-Dimethylheptane
[926-82-9] **C_9H_{20}**



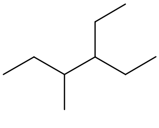
†3196. 4,4-Dimethylheptane
[1068-19-5] **C_9H_{20}**



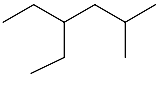
†3197. 3-Ethyl-2,3-dimethylpentane
[16747-33-4] **C_9H_{20}**



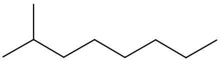
†3198. 3-Ethyl-4-methylhexane
[3074-77-9] **C_9H_{20}**



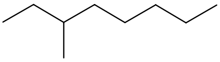
†3199. 4-Ethyl-2-methylhexane
[3074-75-7] **C_9H_{20}**



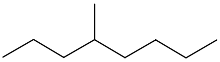
†3200. 2-Methyloctane
[3221-61-2] **C_9H_{20}**



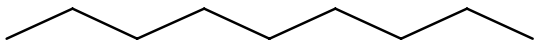
†3201. 3-Methyloctane
[2216-33-3] **C_9H_{20}**



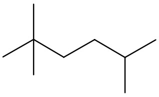
†3202. 4-Methyloctane
[2216-34-4] **C_9H_{20}**



†3203. Nonane
[111-84-2] **C_9H_{20}**



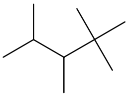
†3204. 2,2,5-Trimethylhexane
[3522-94-9] **C_9H_{20}**



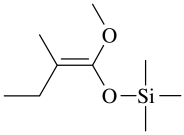
†3205. 2,2,3,3-Tetramethylpentane
[7154-79-2] **C_9H_{20}**

Me_3CCMe_2Et

†3206. 2,2,3,4-Tetramethylpentane
[1186-53-4] **C_9H_{20}**



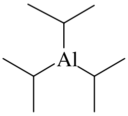
3207. 1-Methoxy-2-methyl-1-(trimethylsilyloxy)-1-butene
([(1-Methoxy-2-methyl-1butenyl)oxy]trimethylsilane)
[84393-12-4] **$C_9H_{20}O_2Si$**



Bromoanisole, Sodamide

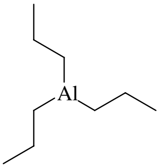
See Sodamide: Aryl halide, 1-Alkoxy-1-(trimethylsilyloxy)alkenes

3208. Triisopropylaluminium
[2397-67-3] **$C_9H_{21}Al$**



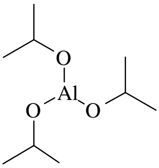
See entry TRIALKYLALUMINIUMS

3209. Tripropylaluminium
[102-67-0] **$C_9H_{21}Al$**



See entry TRIALKYLALUMINIUMS

3210. Aluminium isopropoxide
[555-31-7] **$C_9H_{21}AlO_3$**



Crotonaldehyde, 2-Propanol

See 2-Propanol: Aluminium isopropoxide, etc.

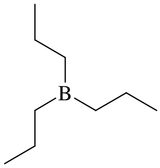
Hydrogen peroxide

See Hydrogen peroxide: Aluminium isopropoxide

See other METAL ALKOXIDES

3211. Tripropylborane

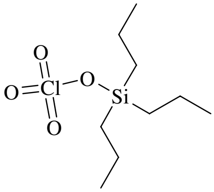
[1116-61-6] **$C_9H_{21}B$**



Gibson, 1969, 147
It ignites in air.
See other ALKYLBORANES

3212. Tripropylsilyl perchlorate

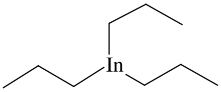
[ ] **$C_9H_{21}ClO_4Si$**



See entry ORGANOSILYL PERCHLORATES

3213. Tripropylindium

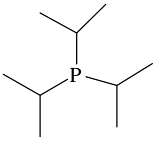
[3015-98-3] **$C_9H_{21}In$**



Leleu, *Cahiers*, 1977, (88), 367
It ignites in air.
See other ALKYLMETALS

3214. Triisopropylphosphine

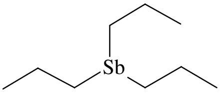
[6476-36-4] **$C_9H_{21}P$**



Chloroform, or Oxidants
Catalogue entry, Deutsche Advance Produktion, 1968

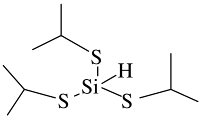
Particularly this phosphine reacts, when undiluted, rather vigorously with most peroxides, ozonides, *N*-oxides, and also chloroform. It may be safely destroyed by pouring into a solution of bromine in carbon tetrachloride.
See other ALKYLPHOSPHINES

3215. Tripropylantimony
[5613-69-4] **$C_9H_{21}Sb$**



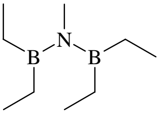
Gibson, 1969, 171
The solid ignites or chars when exposed to air on filter paper.
See other ALKYLMETALS

3216. Tris(2-propylthio)silane
[17891-55-3]] **$C_9H_{22}S_3Si$**



Lambert, J. A., *J. Amer. Chem. Soc.*, 1988, **110**, 2210
The silane, prepared by reduction of tris(2-propylthio)silylenium perchlorate with diisobutylaluminium hydride at —78°C, is subsequently isolated by high-vacuum distillation from the mixture. Heating must be very mild to prevent explosion.
See related ALKYLSILANES

3217. *N,N*-Bis(diethylboryl)methylamine
[19162-21-1] **$C_9H_{23}B_2N$**

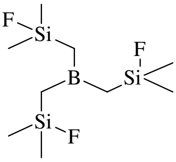


491M, 1975, 258

It ignites in air.
See related ALKYLBORANES

3218. Tris(dimethylfluorosilylmethyl)borane

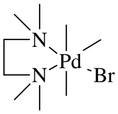
[62497-91-0] **$C_9H_{24}BF_3Si_3$**



Hopper, S. P. *et al., Synth. React. Inorg. Met.-Org. Chem.*, 1976, **6**, 378
The crude or pure material will ignite in air, especially if exposed on filter paper or a similar extended surface.
See related ALKYLBORANES, ALKYLHALOSILANES

3219. *N,N,N′,N′*-Tetramethylethane-1,2-diamine,trimethylpalladium(IV) bromide (Bromotrimethyl-*N,N,N′,N′*-tetramethylethanediamine-*N,N′*-palladium)

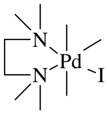
[123147-95-5] **$C_9H_{25}BrN_2Pd$**



De Graaf, W. *et al., Organometallics*, 1990, **9**(5), 1479
Decomposes explosively when heated to 50°C.
See other AMMINEMETAL HALIDES
See related PLATINUM COMPOUNDS

3220. *N,N,N,N*-Tetramethylethane-1,2-diamine,trimethylpalladium(IV) iodide

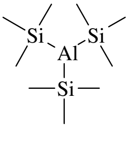
[123147-84-2] **$C_9H_{25}IN_2Pd$**



De Graaf, W. *et al., Organometallics*, 1989, **8**(12), 2907
Decomposes explosively when brought to room temperature.
See other AMMINEMETAL HALIDES
See related PLATINUM COMPOUNDS

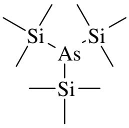
3221a. Tris(trimethylsilyl)aluminium

[65343-66-0] **$C_9H_{27}AlSi_3$**



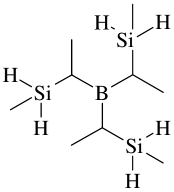
Rösch, L., *Angew. Chem. (Intern. Ed.)*, 1977, **16**, 480
The crystalline solid ignites in air.
See related ALKYLSILANES

3221b. Tris(trimethylsilyl)arsine
[17729-30-5] **$C_9H_{27}AsSi_3$**



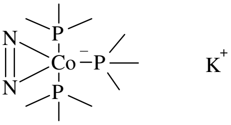
Wills, R. *et al., Inorg. Synth.*, 1997, **31**, 15
Pyrophoric.
See related ALKYLSILANES

3221c. Tris[1-(methylsilyl)ethyl]borane
[224562-17-8] **$C_9H_{27}BSi_3$**



See Tris(1-silylethyl)borane

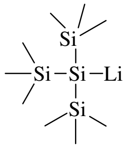
3222a. Potassium dinitrogentris(trimethylphosphine)cobaltate(1—)
[63181-09-9] **$C_9H_{27}CoKN_2P_3$**



Hammer, R. *et al., Angew. Chem. (Intern. Ed.)*, 1977, **16**, 485
The crystalline solid ignites immediately on exposure to air.
See related ALKYLPHOSPHINES, N-METAL DERIVATIVES

3222b. Tris(trimethylsilyl)silyllithium

[4110-02-5] **$C_9H_{27}LiSi_4$**



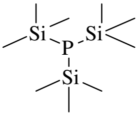
Bochmann, M. *et al., Inorg. Synth.*, 1997, **31**, 162

This compound was obtained as tetrahydrofuran complexes of two and three molecules of solvation. They were mildly pyrophoric.

See related ALKYLSILANES

3223. Tris(trimethylsilyl)phosphine

[15573-38-3] **$C_9H_{27}PSi_3$**



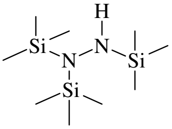
Dahl, O., *Acta Chem. Scand. Ser. B*, 1976, **30**, 799

It is pyrophoric.

See related ALKYLSILANES

3224. Tris(trimethylsilyl)hydrazine

[13272-02-1] **$C_9H_{28}N_2Si_3$**



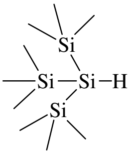
Oxidants

It is hypergolic with fluorine or fuming nitric acid, and explodes with ozone.

See entry SILYLHYDRAZINES

3225. Tris(trimethylsilyl)silane (1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilane)

[1873-77-4] **$C_9H_{28}Si_4$**



Ethyl propynoate, Oxygen

Liu, Y *et al., J. Org. Chem.*, 2005, **70**(2), 556

Mixing the two organics on millimolar scale under an oxygen atmosphere caused an explosion. The experimenters believe that addition of the silane to the triple bond is oxygen initiated. The propynoate will surely have been within flammable limits in the headspace, even if the silane were not.

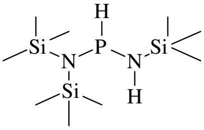
Preparative hazard

Dickhaut, J. *et al., Org. Synth.,* 1992, **70**, 164

The solid residue of the preparation from lithium powder, trimethylsilyl chloride, tetrachlorosilane and methyllithium may be highly pyrophoric. Caution in quenching into dilute acid is advised.

See other ALKYLSILANES

3226. *N,N,N′*-Tris(trimethylsilyl)diaminophosphine
[63104-54-1] **$C_9H_{29}N_2PSi_3$**

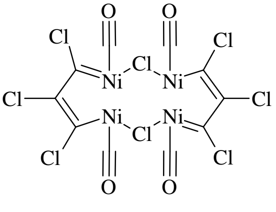


Niecke, E. *et al., Angew. Chem. (Intern. Ed.)*, 1977, **16**, 487

The finely divided solid ignites in air.

See related ALKYLSILANES, PHOSPHINES

3227. Dicarbonyl-η-trichloropropenyldinickel chloride dimer
[64297-36-5] **$C_{10}Cl_8Ni_4O_4$**

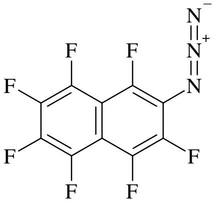


Posey, R. G. *et al. J. Amer. Chem. Soc.*, 1977, **99**, 4865 (footnote 13)

Nickel carbonyl and tetrachloropropadiene react in a wide variety of solvents to give the crystalline title compound which is extremely shock-sensitive, and explodes if touched when dry.

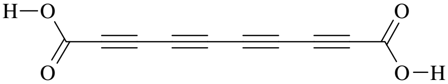
See related CARBONYLMETALS

3228. 2-Azidoperfluoronaphthalene
[74415-60-4] **$C_{10}F_7N_3$**



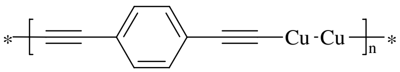
Banks, R. E. *et al., J. Chem. Soc., Chem. Comm.*, 1980, 151
Thermolyses at 300°C/7 mbar to give 2-cyanoperfluoroindene were terminated by explosions.
See other ORGANIC AZIDES

3229. Octatetrayne-1,8-dicarboxylic acid
[40575-26-6] **$C_{10}H_2O_4$**



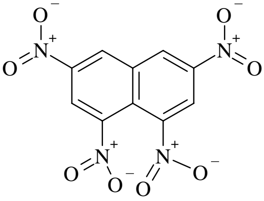
Sorbe, 1968, 151
An explosive solid, extremely heat-sensitive.
See other ACETYLENIC COMPOUNDS, ORGANIC ACIDS

3230. Copper(I) benzene-1,4-bis(ethynide)
[40575-26-6] **$(C_{10}H_4Cu_2)_n$**



Royer, E. C. *et al., J. Inorg. Nucl. Chem.*, 1981, **43**, 708
Explosive, and pyrophoric at 200°C.
See other METAL ACETYLIDES

3231a. 1,3,6,8-Tetranitronaphthalene
[28995-89-3] **$C_{10}H_4N_4O_8$**

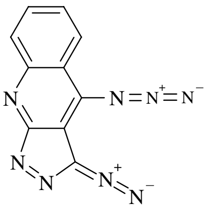


Sorbe, 1968, 151

An explosive solid, most sensitive to heating.
See other POLYNITROARYL COMPOUNDS

3231b. 4-Azido-3-diazo-3*H*-pyrazolo[3,4-b]quinoline

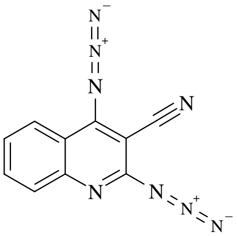
[310898-75-0] **$C_{10}H_4N_8$**



Stadlbauer, W. *et al., J. Chem. Soc., Perk. I*, 2000, (18), 3085
Prepared by diazotisation of the corresponding amino-hydrazino-compound, this material exploded on heating above 110°C. It had an enthalpy of decomposition of around 1.5 kJ/g.

3231c. 2,4-Diazidoquinoline-3-carbonitrile (2,4-Diazido-3-cyanoquinoline)

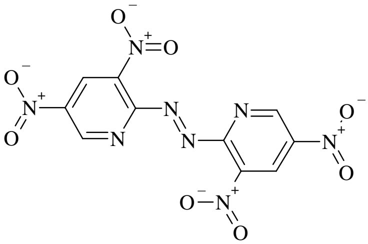
[246546-92-9] **$C_{10}H_4N_8$**



Stadlbauer, W. *et al., J. Chem. Soc., Perk. I*, 2000, (18), 3085
A literature preparation of this compound by diazotisation of 3-amino-4-hydrazino-1*H*-pyrazolo[3,4-b]quinoline was found to give the still more energetic isomer 4-azido-3-diazo-3*H*-pyrazolo[3,4-b]quinoline.
See 4-Azido-3-diazo-3*H*-pyrazolo[3,4-b]quinoline

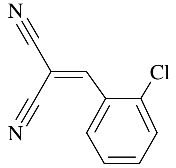
3232a. 2,2′-Azo-3,5-dinitropyridine

[55106-91-7] **$C_{10}H_4N_8O_8$**



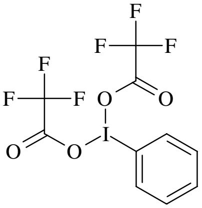
Explosive.
See entry POLYNITROAZOPYRIDINES
See other AZO COMPOUNDS, POLYNITROARYL COMPOUNDS

3232b. 2-Chlorobenzylidenemalononitrile ('CS gas')
[2698-41-1] **$C_{10}H_5ClN_2$**



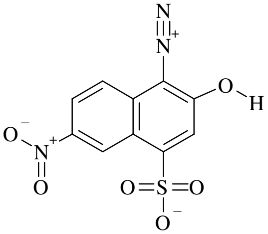
The finely powdered nitrile is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)
See other CYANO COMPOUNDS

3233. [*I,I*-Bis(trifluoroacetoxy)iodo]benzene
[2712-78-9] **$C_{10}H_5F_6IO_4$**



Increase in pH converts the title compound into an explosive 'dimer'.
See 3,5-Dimethyl-4[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole
See μ-Oxo*I,I*-bis(trifluoroacetato-*O*)-*I,I*-diphenyldiiodine(III)
See other I,I-(DIBENZOYLPEROXY)ARYLIODINESIODINE COMPOUNDS

3234. 2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate
[5366-84-7] **$C_{10}H_5N_3O_6S$**

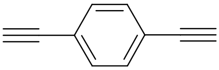


HCS 1980, 362

Fast smouldering propagation occurs on heating the powder moderately.

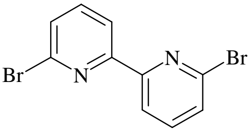
See entry HIGH RATE DECOMPOSITION
See related DIAZONIUM CARBOXYLATES

3235a. 1,4-Diethynylbenzene
[935-14-8] **$C_{10}H_6$**



Preparative hazard
See 1,4-Bis(1,2-dibromoethyl)benzene: Potassium hydroxide
See other ALKYNES

3235b. 6,6′-Dibromo-2,2′-bipyridyl (6,6′-Dibromo-2,2′-bipyridine)
[49669-22-9] **$C_{10}H_6Br_2N_2$**

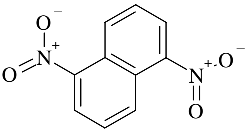


Preparative hazard

1. Nagata, T., Chem. Eng. News, 2000, 78(48), 2
2. Editor's comment

A standard preparation of the above from 2,6-dibromopyridine, by a coupling involving bubbling oxygen through a heavily cooled solution of this and butyllithium in the presence of copper (II) salts, exploded violently on addition of hydrochloric acid for work-up. The reaction was being performed on a smaller scale than previously described [1]. The explosion was attributed to peroxides. Since it is not usual for academic preparations to specify gas flows, over-oxidation, and evaporation of solvent, are always possible in such cases – and perhaps more probable if scaling down while still using a standard size gas inlet [2].

3236. 1,5-Dinitronaphthalene
[605-71-0] **$C_{10}H_6N_2O_4$**



Sulfur, Sulfuric acid
Hub, L., *Proc. Chem. Process Haz. Symp. VI*, (Manchester, 1977), No. 49, 43, Rugby, IChE, 1977
For industrial conversion to 5-aminonaphthoquinone derivatives, dinitronaphthalene had been mixed cold with sulfuric acid and sulfur (to form sulfur dioxide), then heated

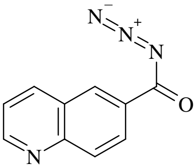
to 120°C on over 100 occasions without incident. When dinitronaphthalene from a different supplier was used, the mixture exploded violently. Investigation in the safety calorimeter showed that an exothermic reaction begins at only 30°C, and that the onset and intensity of the exotherm (up to 400°C) markedly depends on quality of the dinitronaphthalene.

See REACTION SAFETY CALORIMETRY

See other POLYNITROARYL COMPOUNDS

3237. 6-Quinolinecarbonyl azide

[78141-00-1] **$C_{10}H_6N_4O$**



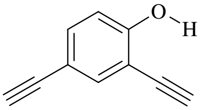
Houben-Weyl, 1952, Vol. 8, 682

A sample heated above its m.p. (88°C) exploded violently.

See other ACYL AZIDES

3238. 2,4-Diethynylphenol

[30427-53-3] **$C_{10}H_6O$**



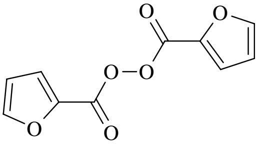
Kotlyarevskii, I. L. *et al., Chem. Abs.*, 1971, **74**, 53198

Oxidation of the methyl or propyl ethers gave insoluble polymeric solids which exploded on heating.

See other ACETYLENIC COMPOUNDS, POLYPEROXIDES

3239. Di-2-furoyl peroxide

[25639-45-6] **$C_{10}H_6O_6$**

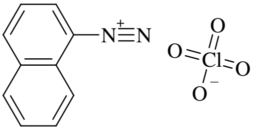


Castrantas, 1965, 17

It explodes violently on friction and heating.

See other DIACYL PEROXIDES

3240. 1-Naphthalenediazonium perchlorate
[68597-02-4] **$C_{10}H_7ClN_2O_4$**

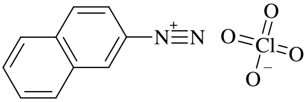


Hofmann, K. A. *et al., Ber.*, 1906, **39**, 3146

Both salts explode under light friction or pressure when dry.

See other DIAZONIUM PERCHLORATES

3241. 2-Naphthalenediazonium perchlorate
[68597-03-5] **$C_{10}H_7ClN_2O_4$**

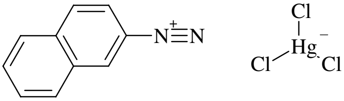


Hofmann, K. A. *et al., Ber.*, 1906, **39**, 3146

Both salts explode under light friction or pressure when dry.

See other DIAZONIUM PERCHLORATES

3242. 2-Naphthalenediazonium trichloromercurate
[68448-47-5] **$C_{10}H_7Cl_3HgN_2$**

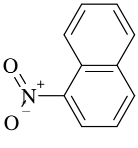


Nesmeyanov, A. M., *Org. Synth.*, 1943, Coll. Vol. 2, 433

The isolated double salt precipitated by mercury(II) chloride explodes violently if heated during drying.

See other DIAZONIUM SALTS, MERCURY COMPOUNDS

3243. 1-Nitronaphthalene
[86-57-7] **$C_{10}H_7NO_2$**



Nitric acid, Sulfuric acid

See Nitric acid: 1-Nitronaphthalene, Sulfuric acid

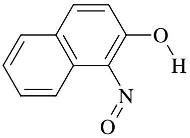
Tetranitromethane

See Tetranitromethane: Aromatic nitro compounds

See other NITROARYL COMPOUNDS

3244. 1-Nitroso-2-naphthol

[131-91-9] **$C_{10}H_7NO_2$**



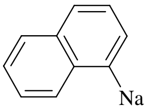
1. Starobinskii, V. A. *et al., Chem. Abs.*, 1980, **92**, 7828
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
3. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987
4. *CHETAH*, 1990, 187

1-Nitroso-2-naphthol, an intermediate in the preparation of ‘Pigment green’, undergoes an exothermic rearrangement at 124°C to an unstable material which appears to ignite spontaneously. Pigment green (an iron complex of a bisulfite derivative of the title compound precipitated with sodium carbonate in presence of additives) decomposes at 230°C with a large exotherm, and the instances of ignition observed during drying of the pigment may be connected with the presence of some free nitrosonaphthol in it [1]. Energy of decomposition (in range 110—180°C) measured by DSC as 1.409 kJ/g by DSC, and T_{ait24} was determined as the low figure of 78°C by adiabatic Dewar tests, with an apparent energy of activation of 209 kJ/mol [2]. The solid deflagrates at 0.74 cm/min, and will attain a maximum of 68 bar pressure in a closed system [3]. It is shock sensitive [4].

See other NITROSO COMPOUNDS, SELF-HEATING AND IGNITION INCIDENTS

3247. Naphthylsodium

[25398-08-7] **$C_{10}H_7Na$**



Chlorinated biphenyl

MCA Case History No. 565

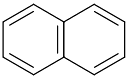
A chlorinated biphenyl heat-transfer liquid was added to a burning batch of naphthylsodium to help to extinguish it. An exothermic reaction, followed by an explosion occurred. Sodium is known to react violently with many halogenated materials.

See Sodium: Halocarbons

See other ARYLMETALS

3248. Naphthalene

[91-20-3] **$C_{10}H_8$**



(*MCA SD-58*, 1956); *NSC 370*, 1978; *FPA H69*, 1978; *HCS 1980*, 672

Zavetskii, A. D., *Chem. Abs.*, 1983, **98**, 128923
Fires inside wood-packed benzene scrubbers in coke oven gas plants were attributed to saturation of the wood with naphthalene, and vapour-phase oxidation of the latter to phthalic anhydride, which participates in exothermic free radical chain reactions.

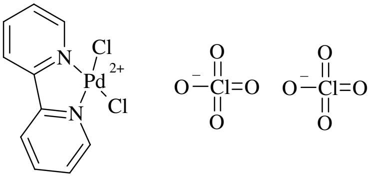
Aluminium chloride, Benzoyl chloride
See Aluminium chloride: Benzoyl chloride, etc.

Dinitrogen pentaoxide
See Dinitrogen pentaoxide: Naphthalene

Other reactants
Yoshida, 1980, 266
MRH values calculated for 13 combinations with oxidants are given.

3249. 2,2′-Bipyridyldichloropalladium(IV) perchlorate

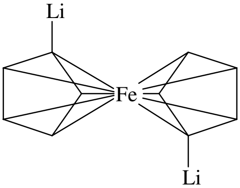
[14871-92-2] (ion) **$C_{10}H_8Cl_4N_2O_8Pd$**



Gray, L. R. *et al., J. Chem. Soc., Dalton Trans.*, 1983, 133—141
Though no explosions occurred during preparation (by addition of 72% perchloric acid to solutions of the complex in conc. nitric/hydrochloric mixtures), this and related amino and phosphino analogues are potentially unstable.
See other AMMINEMETAL OXOSALTS

3250a. μ,1,1′-Ferrocenediyldilithium (Dilithioferrocene)

[33272-09-2] [174872-99-2] tetramethylethanediamine complex **$C_{10}H_8FeLi_2$**



Anhydrides

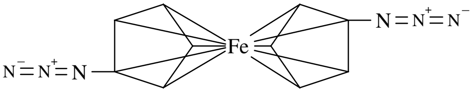
Rulkens, R. *et al., J. Amer. Chem. Soc.*, 1997, **119**(45), 10976

A synthetic procedure was devised which involved mixing this organometallic, as its TMEDA complex, with either solid benzenesulphonothioic acid anhydrosulphide $(PhSO_2)_2S$, or the equivalent selenide, at liquid nitrogen temperatures, and adding tetrahydrofuran. The first few drops of THF, which presumably allowed the dog to see the rabbit, produced vigorous interaction, with possible pressure generation. Reacting anhydrides with alkyl metals, in absence of diluents, may surely be expected to be violent.

See other ALKYLMETALS

3250b. 1,1′-Diazidoferrocene

[94468-22-1] **$C_{10}H_8FeN_6$**



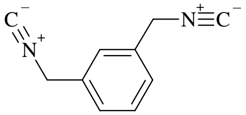
Shafir, A. *et al., Organometallics*, 2000, **19**(19), 3978

Although slow heating gives a sharp melting point of 58°C, rapid heating causes explosion at about this temperature. Preparation on multi-gram scale is not advised.

See other ORGANIC AZIDES

3251. 1,3-Bis(isocyanomethyl)benzene

[ ] **$C_{10}H_8N_2$**

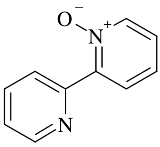


See entry DIISOCYANIDE LIGANDS

See related CYANO COMPOUNDS

3252. 2,2′-Bipyridyl 1-oxide

[33421-43-1] **$C_{10}H_8N_2O$**



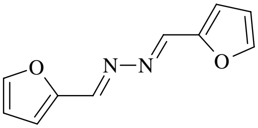
Preparative hazard

See Hydrogen peroxide: Acetic acid, *N*-Heterocycles

See other N-OXIDES

3253. 2-Furaldehyde azine

[5428-37-5] **$C_{10}H_8N_2O_2$**



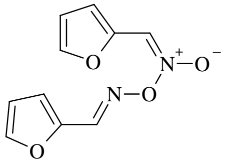
Nitric acid

See Nitric acid: Aromatic amines (reference 5), and : Hydrazines

See related HYDRAZONES

3254. 2,2′-Oxybis(iminomethylfuran) mono-*N*-oxide (Dehydrofurfural oxime)

[ ] **$C_{10}H_8N_2O_4$**



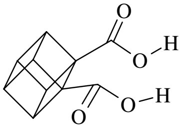
Ponzio, G. *et al., Gazz. Chim. Ital.*, 1906, **36**, 338—344

It explodes at 130°C.

See other N—O COMPOUNDS, N-OXIDES

3255. Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,2-dicarboxylic acid (Cubane-1,2-dicarboxylic acid)

[129103-51-1] **$C_{10}H_8O_4$**



Eaton, P. E. *et al., J. Org. Chem.*, 1990, **55**(22), 5746

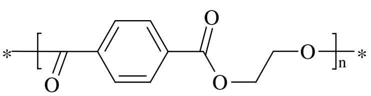
Attempts to dehydrate this to the anhydride were unsuccessful; attempting to distil off monomeric products under vacuum at 80°C after a dehydration attempt with ethoxy-acetylene led to a violent explosion. This is said to be atypical of cubanes, but:

See entry CUBANES

See other STRAINED-RING COMPOUNDS

3256. Poly(ethylene terephthalate)

[25038-59-9] **$(C_{10}H_8O_4)_n$**

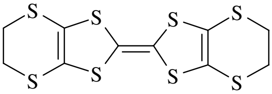


Preparative hazard

See Dimethyl terephthalate: Ethylene glycol, Titanium butoxide

3257. 2,2’-Bi-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiinylidene

[66946-48-3] **$C_{10}H_8S_8$**



Preparative hazard

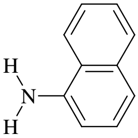
Larsen, J. *et al., Org. Synth.*, 1995, **72**, 265

A procedure avoiding the sometimes explosive reaction of carbon disulfide with alkali metals is detailed.

See Carbon disulfide: Alkali metals

3258. 1-Naphthylamine

[134-32-7] **$C_{10}H_9N$**



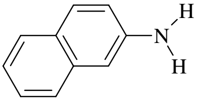
Nitrous acid

See DIAZONIUM SALTS

DIAZONIUM SULFIDES AND DERIVATIVE

3259. 2-Naphthylamine

[91-59-8] **$C_{10}H_9N$**



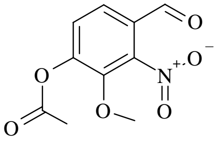
Nitrous acid

See DIAZONIUM SALTS

DIAZONIUM SULFIDES AND DERIVATIVE

3260. 4-Acetoxy-3-methoxy-2-nitrobenzaldehyde

[2698-69-3] **$C_{10}H_9NO_6$**



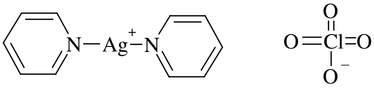
Preparative hazard

See Nitric acid: 4-Acetoxy-3-methoxybenzaldehyde

See other ALDEHYDES, NITROARYL COMPOUNDS

3261. Dipyridinesilver(I) perchlorate (Bispyridinesilver(1+) perchlorate)

[72152-13-7] **$C_{10}H_{10}AgClN_2O_4$**



Acids

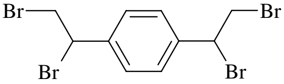
Kauffman, G. B. *et al., Inorg. Synth.*, 1960, **6**, 7, 8

Contact with acids, especially hot, must be avoided to prevent the possibility of violent explosion.

See other AMMINEMETAL OXOSALTS, SILVER COMPOUNDS

3262. 1,4-Bis(1,2-dibromoethyl)benzene

[25393-98-0] **$C_{10}H_{10}Br_4$**



Potassium hydroxide

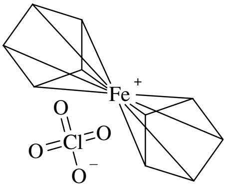
Kotlyarevskii, I. L. *et al., Chem. Abs.*, 1978, **89**, 23858

Tetra-dehydrobromination of the compound in benzene with ethanolic potassium hydroxide for the commercial production of 1,4-diethynylbenzene is highly exothermic and needs careful control to avoid hazard.

See related HALOALKANES

3263. Ferrocenium perchlorate

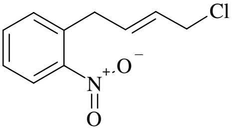
[12312-33-3] **$C_{10}H_{10}ClFeO_4$**



See 1,3-Di[bis(cyclopentadienyl)iron]-2-propen-1-one: Perchloric acid, etc.
See other ORGANOMETALLIC PERCHLORATES

3264. 1-Chloro-4-(2-nitrophenyl)-2-butene

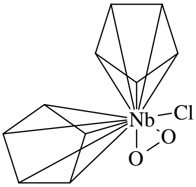
[7318-34-5] **$C_{10}H_{10}ClNO_2$**



Acheson, R. M. *et al., J. Chem. Soc., Perkin Trans. 1*, 1978, 1119
It may explode during distillation at 112—114°C/60 mbar.
See other ALLYL COMPOUNDS, NITROARYL COMPOUNDS

3265. Dicyclopentadienylperoxyniobium chloride

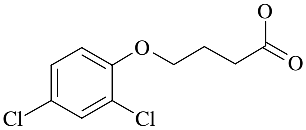
[75109-11-4] **$C_{10}H_{10}ClNbO_2$**



Sala-pala, J. *et al., J. Mol. Catal.*, 1980, **7**, 142—143
The compound and its methyl homologue exploded occasionally when scraped from the walls of a tube, and invariably when exposed to a Raman laser beam, even at —80°C.
See other IRRADIATION DECOMPOSITION INCIDENTS, ORGANOMETALLIC PEROXIDES

3266. 4-(2,4-Dichlorophenoxy)butyric acid

[94-82-6] **$C_{10}H_{10}Cl_2O_3$**

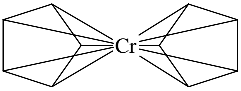


Preparative hazard

See γ-Butyrolactone: 2,4-Dichlorophenol, etc.

3267. Dicyclopentadienylchromium (Chromocene)

[1271-24-5] **$C_{10}H_{10}Cr$**



Alcohols

Votinsky, J. *et al., Coll. Czech. Chem. Comm.*, 1979, **44**, 82

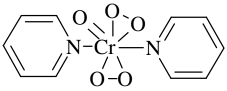
Reaction with C_1—C_4 alcohols at 20°C produces pyrophoric dialkoxychromiums and cyclopentadiene.

See METAL ALKOXIDES

See other ORGANOMETALLICS

3268. Oxodiperoxodipyridinechromium(VI)

[ ] **$C_{10}H_{10}CrN_2O_5$**



1. Caldwell, S. H. *et al., Inorg,. Chem.*, 1969, **8**, 151
2. Adams, D. M. *et al., J. Chem. Educ.*, 1966, **43**, 94
3. Collins, J. C. *et al., Org. Synth.*, 1972, **52**, 5—8
4. Wiede, O. F., *Ber.*, 1897, **30**, 2186
5. Glaros, G., *J. Chem. Educ.*, 1978, **55**, 410

This complex, formerly called ‘pyridine perchromate’ and now finding application as a powerful and selective oxidant, is violently explosive when dry [1]. Use while moist on the day of preparation and destroy any surplus with dilute alkali [2]. Preparation and use of the reagent have been detailed further [3]. The analogous complexes with aniline, piperidine and quinoline may be similarly hazardous [4]. The damage caused by a 1 g sample of the pyridine complex exploding during desiccation on a warm day was extensive. Desiccation of the aniline complex had to be at ice temperature to avoid violent explosion [4]. Pyridinium chlorochromate is commercially available as a safer alternative oxidant of alcohols to aldehydes [5].

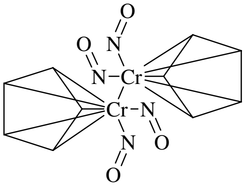
Dipyridinium dichromate

See Chromium trioxide: Pyridine

See other AMMINECHROMIUM PEROXOCOMPLEXES

3269. Bis(cyclopentadienyldinitrosylchromium)

[66649-16-9] **$C_{10}H_{10}Cr_2N_4O_4$**



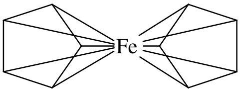
Flitcroft, N. *et al., Chem. & Ind.*, 1969, 201

A small sample exploded violently upon laser irradiation for Raman spectroscopy.

See other IRRADIATION DECOMPOSITION INCIDENTS, ORGANOMETALLICS

3270a. Ferrocene

[102-54-5] **$C_{10}H_{10}Fe$**



Mercury(II) nitrate

See Mercury(II) nitrate: Ferrocene

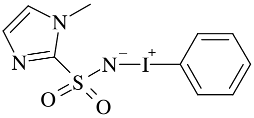
Tetranitromethane

See Tetranitromethane: Ferrocene

See other ORGANOMETALLICS

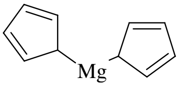
3270b. (1-Methylimidazol-2-ylsulfonyliminoiodo)benzene ([[(1-Methyl-1H-imidazol-2-yl)sulfonyl]aminophenyl]iodonium, inner salt)

[243467-02-9] **$C_{10}H_{10}IN_3Mg_2S$**



3271. Bis(cyclopentadienyl)magnesium

[1284-72-6] **$C_{10}H_{10}Mg$**



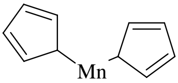
Barber, W. A., *Inorg. Synth.*, 1960, **6**, 15

It may ignite on exposure to air.

See other ORGANOMETALLICS

3272. Bis(cyclopentadienyl)manganese

[1271-27-8] **$C_{10}H_{10}Mn$**

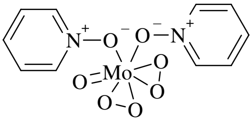


491M, 1975, 248

It ignites in air.
See other ORGANOMETALLICS

3273. Oxodiperoxodi(pyridine *N*-oxide)molybdenum

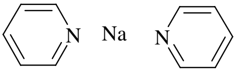
[73680-23-6] **$C_{10}H_{10}MoN_2O_7$**



Westland, A. D. *et al., Inorg. Chem.*, 1980, **19**, 2257
The analogous complex of tungsten, and that of chromium with a single *N*-oxide ligand, were also explosive.
See related AMMINECHROMIUM PEROXOCOMPLEXES

3274. Dipyridinesodium

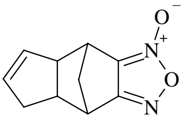
[101697-88-5] **$C_{10}H_{10}N_2Na$**



Sidgwick, 1950, 89
The addition product of sodium and pyridine (or its 2-methyl derivative) ignites in air.
See related N-METAL DERIVATIVES

3275. 4a,5,7a,8-Tetrahydro-4,8-methano-4*H*-indeno[5,6-*c*]-1,2,5-oxadiazole 1-oxide (Dicyclopentadienefurazan *N*-oxide)

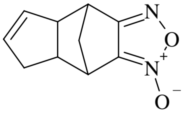
[ ] **$C_{10}H_{10}N_2O_2$**



Crosby, J. *et al.*, Br. Pat. 1 474 693, 1977
The solid isomeric mixture of the 1-oxides explodes at 80—85°C, but may be handled safely in solution.
See other FURAZAN N-OXIDES

3276. 4a,5,7a,8-Tetrahydro-4,8-methano-4*H*-indeno[5,6-*c*]-1,2,5-oxadiazole 3-oxide (Dicyclopentadienefurazan *N*-oxide)

[ ] **$C_{10}H_{10}N_2O_2$**



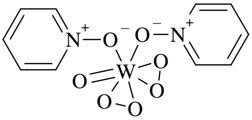
Crosby, J. *et al.*, Br. Pat. 1 474 693, 1977

The solid isomeric mixture of the 3-oxide explodes at 80—85°C, but may be handled safely in solution.

See other FURAZAN N-OXIDES

3277. Oxodiperoxodi(pyridine *N*-oxide)tungsten

[ ] **$C_{10}H_{10}N_2O_7W$**



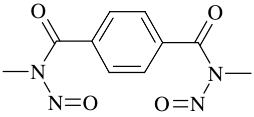
Westland, A. D. *et al., Inorg. Chem.*, 1980, **19**, 2257

The analogous complex of molybdenum, and that of chromium with a single *N*-oxide ligand, were also explosive.

See related AMMINECHROMIUM PEROXOCOMPLEXES

3278. *N,N′*-Dimethyl-*N,N′*-dinitrosoterephthalamide

[133-55-1] **$C_{10}H_{10}N_4O_4$**



2-Hydroxyethylamine

MCA Case History No. 2308

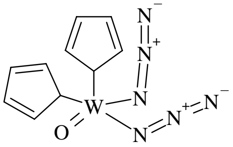
Addition of the dry nitrosamide to a flask apparently containing residual ethanolamine led to evolution and ignition of diazomethane and the dry nitrosamide powder.

See Diazomethane

See other NITROSO COMPOUNDS

3279. Bis(cyclopentadienyl)tungsten diazide oxide

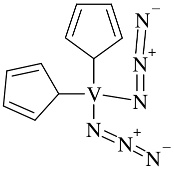
[53504-80-6] **$C_{10}H_{10}N_6OW$**



Anand, S. P., *J. Inorg. Nucl. Chem.*, 1974, **36**, 926
It is highly explosive.
See related METAL AZIDES

3280. Bis(cyclopentadienyl)vanadium diazide

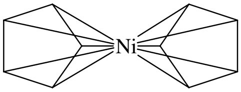
[85836-55-1] **$C_{10}H_{10}N_6V$**



Blandy, C. *et al., Tetrahedron. Lett.*, 1983, **24**, 4189—4192
It is explosive in the solid state.
See related METAL AZIDES

3281. Nickelocene

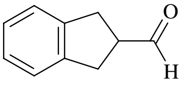
[1271-28-9] **$C_{10}H_{10}Ni$**



See 1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene
See other ORGANOMETALLICS

3282. 2-Indanecarboxaldehyde

[37414-44-1] **$C_{10}H_{10}O$**

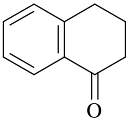


1. Black, T. H., *Chem. Eng. News*, 1988, **66**(32), 2
2. Black, T. H., private comm., 1988

A violent explosion occurred at the start of bulb-tube distillation of a 2 g sample of the crude aldehyde (b.p. 97°/4 mbar) at 75°C/0.13 mbar [1]. It seems likely that the crude product could have formed peroxide during the 2 day's storage (in a closed but not

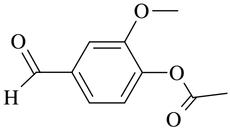
hermetically sealed vessel) between preparation and distillation. The structure is such that the proton on C-2, which effectively has 2 benzyl substituents and an adjacent carbonyl function, seems rather susceptible to autoxidation [2].
See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

3283. 1-Oxo-1,2,3,4-tetrahydronaphthalene
[529-34-0] **$C_{10}H_{10}O$**



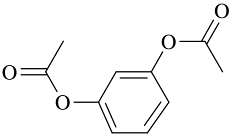
Preparative hazards
See Chromium trioxide: Acetic anhydride
Hydrogen peroxide: Acetone, etc.

3284. 4-Acetoxy-3-methoxybenzaldehyde
[881-68-5] **$C_{10}H_{10}O_4$**



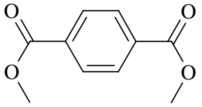
Nitric acid
See Nitric acid: 4-Acetoxy-3-methoxybenzaldehyde
See other ALDEHYDES

3285. 1,3-Diacetoxybenzene (Resorcinol diacetate)
[108-58-7] **$C_{10}H_{10}O_4$**



Nitric acid
See 4,6-Dinitro-1,3-benzenediol

3286. Dimethyl terephthalate
[120-61-6] **$C_{10}H_{10}O_4$**



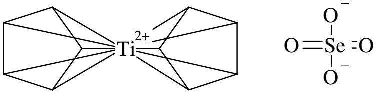
The finely powdered ester is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

Ethylene glycol, Titanium butoxide

1. Rix, G. C., private comm., 1977
2. Goodman, I. in *Encyclopaedia of Polymer Science and Technology*, Mark, H. F. (Ed.), Vol. 11, 112—113, New York, Interscience, 1969

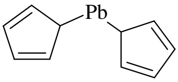
The polymer had been produced for 12 years by transesterification under nitrogen of the dimethyl ester with ethylene glycol at 250°C in presence of titanium butoxide catalyst. After increasing the heating capacity of the vessel from a half coil to a full coil, 3 incidents of ignition of vapour after opening the vessel were noted [1]. This is attributed to formation and ignition of mixtures of acetaldehyde or dioxane with ingressing air on the hot vessel surfaces. Acetaldehyde is produced by thermal degradation of the polymer [2], and has rather wide flammability limits (4—57%) and is readily ignited on hot or corroded surfaces. Dioxane, readily formed by heating ethylene glycol with acids, metal oxides or other catalysts, also has wide limits (2—22%) and a low autoignition temperature (180°C). It seems likely that if either of these were present, perhaps with residual traces of methanol vapour, migration towards an open vent would produce turbulence and admixture with air.
See related SELF-HEATING AND IGNITION INCIDENTS

3287. Bis(cyclopentadienyl)titanium selenate
[87612-48-4] **$C_{10}H_{10}O_4SeTi$**



Malek, J. *et al., Z. Chem.*, 1983, **23**, 189
It is explosive, sensitive to heat or friction.
See other ORGANOMETALLICS
See related ORGANOMETALLIC NITRATES

3288. Bis(cyclopentadienyl)lead
[1294-74-2] **$C_{10}H_{10}Pb$**

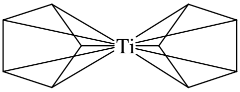


Preparative hazard

See Lead(II) nitrate: Cyclopentadienylsodium

See other ORGANOMETALLICS

3289. Bis(cyclopentadienyl)titanium (Titanocene)
[1271-29-0] $C_{10}H_{10}Ti$



Bailar, 1973, Vol. 3, 389

Pyrophoric crystals (but see Polar solvents, below).

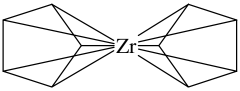
Polar solvents

Watt, G. W. *et al., J. Amer. Chem. Soc.*, 1966, **88**, 1139—1140

Though not pyrophoric, it reacts very vigorously with oxygen-free water and other polar solvents.

See other ORGANOMETALLICS

3290. Bis(cyclopentadienyl)zirconium
[12116-83-5] $C_{10}H_{10}Zr$

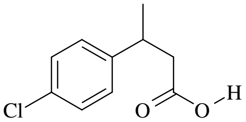


Watt, G. W. *et al., J. Amer. Chem. Soc.*, 1966, **88**, 5926

A pyrophoric solid.

See other ORGANOMETALLICS

3291. 3-(4-Chlorophenyl)butanoic acid
[1012-17-5] $C_{10}H_{11}ClO_2$



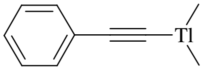
Preparative hazard

See Peroxyacetic acid: 5-(4’-Chlorophenyl)-2,2-dimethyl-3-hexanone

See other ORGANIC ACIDS

3292. Dimethyl(phenylethynyl)thallium

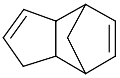
[10158-43-7] **$C_{10}H_{11}Tl$**



Nast, R. *et al., J. Organomet. Chem.*, 1966, **6**, 461
May explode on stirring, heating or impact.
See other ALKYLMETALS, METAL ACETYLIDES

†3293. Dicyclopentadiene

[77-73-6] **$C_{10}H_{12}$**



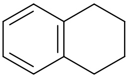
HCS 1980, 387

1. Ahmed, M., *et al., Plant/Oper. Progr.*, 1991, **10**(3), 143
2. Wakakura, M. *et al., J. Loss Prev. Process Ind.*, 1999, **12**, 84

The compound is capable of exothermic pressure generating decompositions, from about 170°C [1]. A short account of an explosion in a tank(?) used for polymerisation. It is thought that excess catalyst (diethylaluminium chloride) caused the polymerisation to run out of control. It should have been at 55°C but reached 234°C and 5.4 MPa[2].
See other DIENES, GAS EVOLUTION INCIDENTS

3294. Tetrahydronaphthalene

[119-64-2] **$C_{10}H_{12}$**



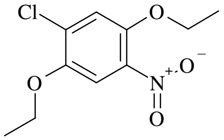
HCS 1980, 893; *RSC Lab. Hazards Safety Data Sheet No. 78*, 1989

1. Grignard, 1949, Vol. 17.1, 673
2. Duckworth, D. F., private comm., 1977
3. McDonald, J. S., *Chem. Abs.*, 1960, **54**, 15933

Readily peroxidises in air, and explosions have occurred during large-scale distillations [1], particularly towards the end when sufficiently concentrated [2]. Use of tetralin as secondary coolant in a molten sodium heat transfer system led to an explosion due to peroxide formation [3].
See 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide
See other PEROXIDISABLE COMPOUNDS

3295. 4-Chloro-2,5-diethoxynitrobenzene

[91-43-0] **$C_{10}H_{12}ClNO_4$**



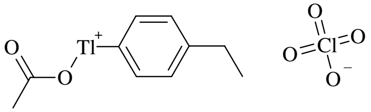
CHETAH, 1990, 183

Although not sensitive to mechanical shock, this compound can be exploded by a detonator.

See other HALOARYL COMPOUNDS, NITROARYL COMPOUNDS

3296. Ethylphenylthallium(III) acetate perchlorate

[34521-47-6] **$C_{10}H_{12}ClO_6Tl$**



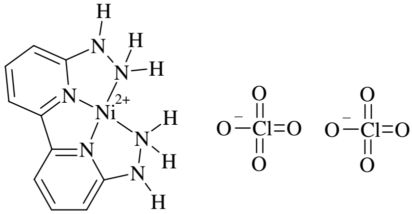
Preparative hazard

See Perchloric acid: Ethylbenzene, Thallium triacetate

See related METAL PERCHLORATES

3297. 6,6′-Dihydrazino-2,2′-bipyridylnickel(II) perchlorate

[53346-21-7] **$C_{10}H_{12}Cl_2N_6NiO_8$**



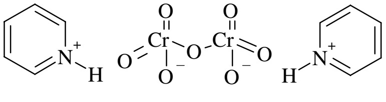
Lewis, J. *et al., J. Chem. Soc., Dalton Trans.*, 1977, 738

It detonates violently on heating, but is stable to shocks.

See other AMMINEMETAL OXOSALTS

3298. Dipyridinium dichromate

[20039-37-6] **$C_{10}H_{12}Cr_2N_2O_7$**



van den Braken, A., *Chem. Eng. News*, 2003, **81**(16) 4

A batch of the oxidant was repackaged into three ~15 kg stainless steel drums, not new but cleaned and dried before use. After an hour the bottom of the three started hissing, then threw forth flame and smoke. An hour later a second also started to deflagrate. The third remained stable. It was possible to extinguish the reaction with water. No similar behaviour could be instituted by dampening the material with water, nor did DSC show any anomalous behaviour.

Preparative hazard

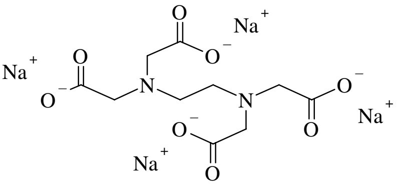
1. Coates, W. M. *et al., Chem. & Ind.*, 1969, 1594
2. Fieser, M. *et al., Reagents for Organic Synth.*, 1981, Vol. 9, 399
3. Corey, E. J. *et al., Tetrahedron Lett.*, 1979, 399
4. Salmon, J., *Chem. & Ind.*, 1982, 616; *Chem. Brit.*, 1982, **18**, 703
5. Gill, P. *et al., Thermochim. Acta*, 1984, **80**, 193—196

It is known that preparation of the oxidant salt under anhydrous conditions is explosion-prone [1], but during repetition of a supposedly safe preparative method [2], recommended for large-scale use [3], ignition and a violent explosion occurred. Use of more water to dissolve completely the chromium trioxide, and a reaction temperature below 25°C, are recommended [4]. During a study by TGA of the thermal degradation of the salt, too-rapid heating of the samples led to explosions with fire [5].

See other DICHROMATE SALTS OF NITROGENOUS BASES, OXIDANTS

3299. Sodium ethylenediaminetetraacetate

[67401-50-7] **$C_{10}H_{12}N_2Na_4O_8$**

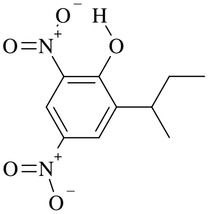


Sodium hydroxide, Sodium hypochlorite

See Sodium hypochlorite: Sodium ethylenediaminetetraacetate, etc.

3300. 4,6-Dinitro-2-*sec*-butylphenol

[88-85-7] **$C_{10}H_{12}N_2O_5$**

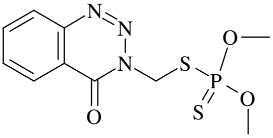


Nolan, 1983, Case history 99

A batch became overheated during drying (leaking steam valve) and decomposed violently.
See other POLYNITROARYL COMPOUNDS

3301. *O,O*-Dimethyl-*S*-[(4-oxo-1,2,3-benxotriazin-3[4*H*]-yl)methyl] phosphorodithioate (Azinphos-methyl)

[86-50-0] **$C_{10}H_{12}N_3O_3PS_2$**

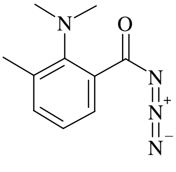


1. Kirschner, E., *Chem. Eng. News*, 1997, **75**(20), 12
2. Joseph, G., *J. Haz. Mat.*, 2003, **104**(1-3), 65

A smouldering bag in a pesticide warehouse, believed to be of this, led to an explosion, killing three firemen, and fire which took six days to extinguish (possibly because of caution concerning anti-cholinesterase toxicity). This is a moderately high energy compound by virtue of the triazene function. Other pesticides present were of less energetic structure [1]. What may be the same accident, and is certainly a similar one, is among the, mostly unrelated, mishaps narrated in [2].
See also THIONOESTERS
See other TRIAZENES

3302. 2-Dimethylamino-3-methylbenzoyl azide

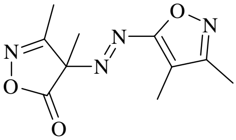
[161616-67-7] **$C_{10}H_{12}N_4O$**



Waldron N. M. *et al., J. Chem. Soc., Chem. Comm.*, 1995, 81
With only 20% azide nitrogen by weight, this azide might be thought safe for cautious isolation. A 1g sample isolated by evaporation of solvent at —10°C, exploded violently and spontaneously on warming to 0°C.
See other ACYL AZIDES

3303. 3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one

[4100-38-3] **$C_{10}H_{12}N_4O_3$**



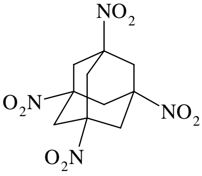
Boulton, A. J. *et al., J. Chem. Soc.*, 1965, 5415

It invariably decomposed explosively if heated rapidly to 100°C, but was stable to impact or friction.

See other AZO COMPOUNDS, ISOXAZOLES, N—O COMPOUNDS

3304. 1,3,5,7-Tetranitroadamantane

[75476-36-7] **$C_{10}H_{12}N_4O_8$**



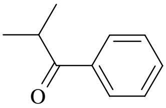
Gilbert, E. E. *et al.*, US Pat. 4 329 522, 1982

It shows explosive properties

See related POLYNITROALKYL COMPOUNDS

3305. Isobutyrophenone

[611-70-1] **$C_{10}H_{12}O$**

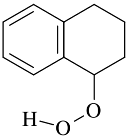


Bromine

See Bromine: Isobutyrophenone

3306. 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide

[771-29-9] **$C_{10}H_{12}O_2$**



Hock, H. *et al., Ber.*, 1933, **66**, 61

It explodes on superheating the liquid.

Lithium tetrahydroaluminate

Sutton, D. A., *Chem. & Ind.*, 1951, 272

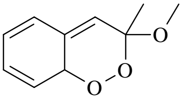
Interaction in ether is vigorously exothermic.

See other REDOX REACTIONS

See related ALKYL HYDROPEROXIDES

3307. 3-Methoxy-3-methyl-5,6-benzo-6*H*-1,2-dioxin

[69681-99-8, cis-; 69682-00-4, trans-**]** $C_{10}H_{12}O_3$



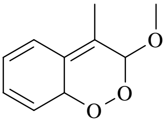
Lerdal, D. *et al., Tetrahedron Lett.*, 1978, 3228

Both isomers decomposed violently on heating in absence of solvent.

See other CYCLIC PEROXIDES

3308. 3-Methoxy-4-methyl-5,6-benzo-6*H*-1,2-dioxin

[69682-01-5] $\mathbf{C_{10}H_{12}O_3}$



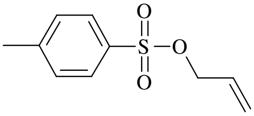
Lerdal, D. *et al., Tetrahedron Lett.*, 1978, 3228

It decomposed violently on heating in absence of solvent.

See other CYCLIC PEROXIDES

3309. Allyl 4-toluenesulfonate

[4873-09-0] $\mathbf{C_{10}H_{12}O_3S}$

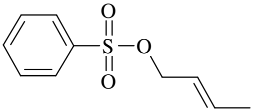


Rüst, 1948, 302

Explosion and charring of the ester during high-vacuum distillation from an oil-bath at 110°C was ascribed to exothermic polymerisation, (probably catalysed by acidic decomposition products).

See other ALLYL COMPOUNDS, POLYMERISATION INCIDENTS, SULFUR ESTERS

3310. 2-Buten-1-yl benzenesulfonate
[20443-67-8] **$C_{10}H_{12}O_3S$**

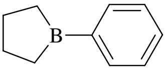


Sorbe, 1968, 122

After evaporation of solvent, the ester may explode in contact with air (possibly owing to exothermic polymerisation catalysed by peroxide formation).

See other POLYMERISATION INCIDENTS, SULFUR ESTERS

3311. 1-Phenylboralane
[1075-17-8] **$C_{10}H_{13}B$**

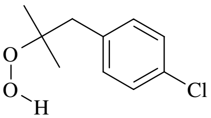


Leleu, *Cahiers*, 1977, (88), 365

It ignites in air.

See related ALKYLBORANES

3312. 2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide
[71356-36-0] **$C_{10}H_{13}ClO_2$**



Preparative hazard

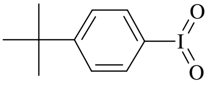
1. Kochi, J. B. *et al., J. Amer. Chem. Soc.*, 1964, **86**, 5268
2. Parris, M. *et al., Can. J. Chem.*, 1979, **57**, 1233—1234

Preparation by the method used for the 2-phenyl analogue [1] is hazardous [2]. (No further details)

See Hydrogen peroxide: 2-Phenyl-1,1-dimethylethanol, etc.

See other ALKYL HYDROPEROXIDES

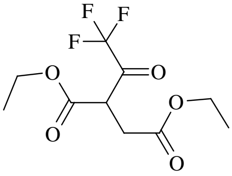
3313. 4-*tert*-Butyliodylbenzene
[64297-75-2] **$C_{10}H_{13}IO_2$**



Ranganathan, S. *et al., Tetrahedron Lett.*, 1985, **26**, 4955—4956

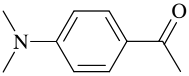
Although a stable crystalline compound (m.p. 217—221°C), its oxidation potential approximates to that of ozone, and it should only be used in a suitably inert solvent (chlorobenzene or nitrobenzene).
See other IODINE COMPOUNDS, OXIDANTS

3314. Diethyl trifluoroacetosuccinate
[94633-25-7] **$C_{10}H_{13}F_3O_5$**



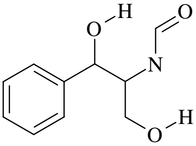
Preparative hazard
See Sodium hydride: Diethyl succinate, etc.

3315. 4-Dimethylaminoacetophenone
[18925-69-4] **$C_{10}H_{13}NO$**



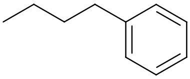
Preparative hazard
See 4-Chloroacetophenone: Dimethylamine

3316. 2-Formylamino-1-phenyl-1,3-propanediol
[51317-78-3] **$C_{10}H_{13}NO_3$**



Nitric acid
See Nitric acid: 2-Formylamino-1-phenyl-1,3-propanediol

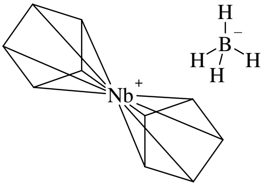
3317. Butylbenzene
[104-51-8] **$C_{10}H_{14}$**



Preparative hazard
See Sodium: Halocarbons (reference 7)

3318. Bis(cyclopentadienyl)niobium tetrahydroborate

[37298-41-2] **$C_{10}H_{14}BNb$**



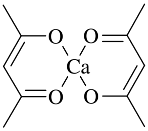
Lucas, C. R., *Inorg. Synth.*, 1976, **16**, 109—110

It is pyrophoric in air, particularly after sublimation.

See other COMPLEX HYDRIDES, ORGANOMETALLICS

3319. Calcium 2,4-pentanedionate

[19372-44-2] **$C_{10}H_{14}CaO_4$**

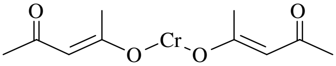


Barium perchlorate

See Barium perchlorate: Calcium 2,4-pentanedionate

3320. Bis(2,4-pentanedionato)chromium

[14024-50-1] **$C_{10}H_{14}CrO_4$**



Ocone, L. R. *et al., Inorg. Synth.*, 1966, **8**, 131

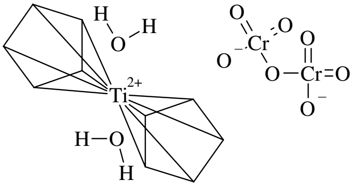
It ignites in air.

See Chromium(II) acetate

See related METAL ALKOXIDES, ORGANOMETALLICS

3321. Diaquabis(cyclopentadienyl)titanium dichromate

[87612-49-5] **$C_{10}H_{14}Cr_2O_9Ti$**



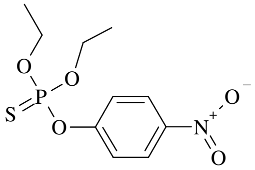
Malek, J. *et al, Z. Chem.*, 1983, **23**, 189

Explosive, sensitive to heat or friction.

See other ORGANOMETALLICS

3322. Diethyl 4-nitrophenyl thionophosphate

[25737-28-4] **$C_{10}H_{14}NO_5PS$**



1. Bright, N. H. F. *et al., J. Agr. Food Chem.*, 1950, **1**, 344
2. Gweek, B. F. *et al., Ind. Eng. Chem.*, 1959, **51**, 104—112
3. Andreozzi, R. *et al., J. Loss Prev.*, 1999, **12**, 315

Vacuum distillation of ‘parathion’ at above 100°C is hazardous, frequently leading to violent decomposition [1]. Following a plant explosion, the process design was modified and featured a high degree of temperature sensing and control to avoid a recurrence [2]. An ARC study of thermal decomposition of ethyl parathion from 150°C is reported. Two separate exotherms are reported (presumably corresponding to isomerisation of the thionophosphate and reduction of the nitro-group). Final temperature and pressure were 360°C and 50 bar with a heat of decomposition of 326 kJ/mole [3].

See THIONOESTERS

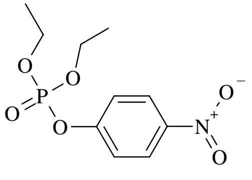
Endrin

During the blending of the two insecticides (endrin is a halogenated polycyclic epoxide) into a petroleum solvent, an unexpected exothermic reaction occurred which vaporised some solvent and led to a vapour—air explosion. Faulty agitation was suspected.

See other AGITATION INCIDENTS, NITROARYL COMPOUNDS, PHOSPHORUS ESTERS

3323. Diethyl 4-nitrophenyl phosphate

[311-45-5] **$C_{10}H_{14}NO_6P$**



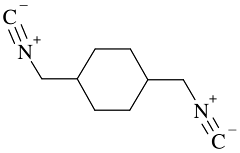
Preparative hazard

See Diethyl phosphite: 4-Nitrophenol

See other NITROARYL COMPOUNDS, PHOSPHORUS ESTERS

3324. 1,4-Bis(isocyanomethyl)cyclohexane

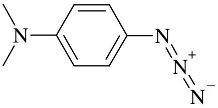
[ ] **$C_{10}H_{14}N_2$**



See entry DIISOCYANIDE LIGANDS

3325. 4-Azido-*N,N*-dimethylaniline

[24573-95-3] **$C_{10}H_{14}N_4$**

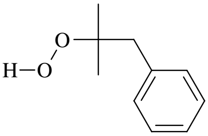


491M, 1975, 51

It decomposed violently on attempted distillation.
See other ORGANIC AZIDES

3326. 2-Phenyl-1,1-dimethylethyl hydroperoxide

[1944-83-8] **$C_{10}H_{14}O_2$**

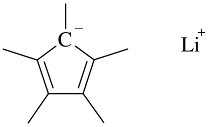


Preparative hazard

See Hydrogen peroxide: 2-Phenyl-1,1-dimethylethanol, etc.
See other ALKYL HYDROPEROXIDES

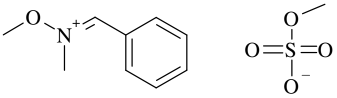
†3327. Pentamethylcyclopentadienyllithium (1,2,3,4,5-Pentamethyl-2,4-cyclopentadien-1-yllithium)

[51905-34-1] **$C_{10}H_{15}Li$**



Manriquez, J. M. *et al., Inorg. Synth.*, 1997, **31**, 214
Pyrophoric
See other ALKYLMETALS

3328. *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate
[ ] **$C_{10}H_{15}NO_5S$**

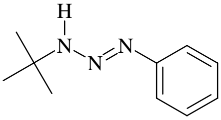


Volpiana, —, *Proc. 1st Int. Symp. Prev. Risks Chem. Ind.*, 176—179, Heidelberg, ISSA, 1970

Quaternation of *O*-methylbenzaldoxime was effected by addition to dimethyl sulfate at 110°C with cooling to maintain that temperature for 2 hours more. Cessation of temperature control allowed a slow exotherm to proceed unnoticed, and at 140—150°C a violent decomposition set in.

See other N—O COMPOUNDS
See related OXIMES

3329. 1-Phenyl-3-*tert*-butyltriazene
[63246-75-3] **$C_{10}H_{15}N_3$**

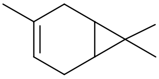


Rondevstedt, C. S. *et al., J. Org. Chem.*, 1957, **22**, 203

It exploded on attempted distillation at below 1 mbar.

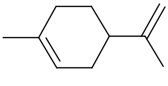
See other TRIAZENES

3330. Δ3-Carene (3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene)
[13466-78-9] **$C_{10}H_{16}$**



Nitric acid
See Nitric acid: Hydrocarbons (reference 15)
See related ALKENES

3331. Limonene (4-Isopropenyl-1-methylcyclohexene)
[5989-27-5] **$C_{10}H_{16}$**



HCS 1980, 591

Iodine pentafluoride, Tetrafluoroethylene

See Tetrafluoroethylene: Iodine pentafluoride, etc.

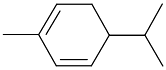
Sulfur

See Sulfur: Limonene

See other DIENES, PEROXIDISABLE COMPOUNDS

3332. 1,5-*p*-Menthadiene (5-Isopropyl-2-methyl-1,3-cyclohexadiene)

[99-83-2] **$C_{10}H_{16}$**



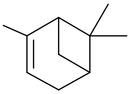
Bodendorf, K., *Arch. Pharm.*, 1933, **271**, 28

The terpene readily peroxidises with air, and the (polymeric) peroxidic residue exploded violently on attempted distillation at 100°C/0.4 mbar.

See other DIENES, PEROXIDISABLE COMPOUNDS, POLYPEROXIDES

3333. 2-Pinene (2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene)

[80-56-8] **$C_{10}H_{16}$**



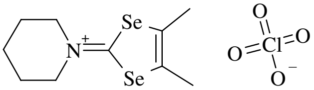
Nitrosyl perchlorate

See Nitrosyl perchlorate: Organic materials

See related ALKENES

3334. 1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate

[53808-74-5] **$C_{10}H_{16}ClNO_4Se_2$**

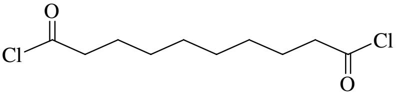


See entry 1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES

See other PERCHLORATE SALTS OF NITROGENOUS BASES

3335. Sebacoyl chloride

[111-19-3] **$C_{10}H_{16}Cl_2O_2$**



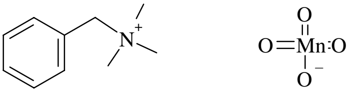
Hüning, S. *et al., Org. Synth.*, 1963, **43**, 37

During vacuum distillation of the chloride at 173°C/20 mbar, the residue frequently decomposes spontaneously, producing a voluminous black foam.

See other ACYL HALIDES

3336. Benzyltrimethylammonium permanganate

[76710-75-3] **$C_{10}H_{16}MnNO_4$**

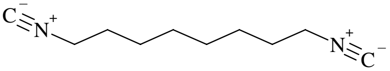


It explodes at 80—90°C.

See entry QUATERNARY OXIDANTS

3337. 1,8-Diisocyanooctane

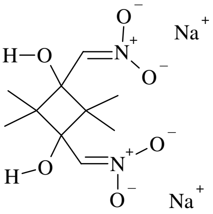
[ ] **$C_{10}H_{16}N_2$**



See entry DIISOCYANIDE LIGANDS

3338. Sodium 1,3-dihydroxy-1,3-bis(*aci*-nitromethyl)-2,2,4,4-tetramethylcyclo-butandiide

[ ] **$C_{10}H_{16}N_2Na_2O_6$**



Water

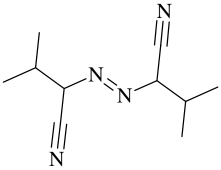
Dauben, H. J., *Org. Synth.*, 1963, Coll. Vol. 4, 223

The dry powdered condensation product of sodium *aci*-nitromethanide (2 mol) with dimethylketene dimer exploded violently when added to crushed ice.

See Sodium *aci*-nitromethanide: Water

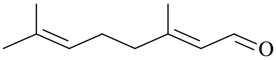
See other ACI-NITRO SALTS

3339. 2,2′-Azoisovaleronitrile
[70843-45-7] **$C_{10}H_{16}N_4$**



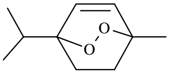
See entry BLOWING AGENTS
See other AZO COMPOUNDS, CYANO COMPOUNDS

3340. 3,7-Dimethyl-2,6-octadienal (Citral)
[5392-40-5] **$C_{10}H_{16}O$**



Preparative hazard
See 2-Methyl-1,3-butadiene: Acetone
See related DIENES

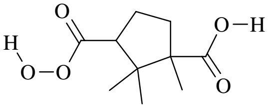
3341. 1,4-Epidioxy-2-*p*-menthene (Ascaridole)
[512-85-6] **$C_{10}H_{16}O_2$**



1. Castrantas, 1965, 15
2. Henry, T. A. *et al., J. Chem. Soc.*, 1921, **119**, 1722
3. Walton, F. P., private comm., 1980

Explosive decomposition occurs on heating from 130 to 150°C [1]. When heated above 160°C, explosive rearrangement occurs with an exotherm to 300°C. An explosion occurred during fractional distillation at 108—110°C/20 mbar. It may be distilled without explosion by a flash evaporation technique [2,3].
See other CYCLIC PEROXIDES

3342. 3-Peroxycamphoric acid (1,2,2-Trimethyl-1-carboxycyclopentane-3-peroxycarboxylic acid)
[31921-03-6] **$C_{10}H_{16}O_5$**



1. Milas, N. A. *et al., J. Amer. Chem. Soc.*, 1933, **55**, 350

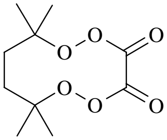
2. Pirkle, W. H. *et al., J. Org. Chem.*, 1977, **42**, 2080—2082

Explosive decomposition occurs at 80—100°C [1], but the isomeric 1-peroxy acid may also have been present in the sample [2].

See other ORGANIC ACIDS, PEROXYACIDS

3343. 7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione (2,5-Dimethyl-2,5-hexylenebis diperoxyoxalate)

[35551-08-7] **$C_{10}H_{16}O_6$**



Preparative hazard

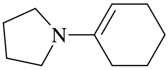
Adam, W. *et al., J. Amer. Chem. Soc.*, 1980, **102**, 4803

The preparation is hazardous because a highly explosive peroxidic polymer is formed as the major product. After extraction of the title product with pentane, the residue must be disposed of forthwith to avoid the possibility of detonation of the polymer as it dries, as happened on one occasion.

See other CYCLIC PEROXIDES, PEROXYESTERS

3344. 1-Pyrrolidinylcyclohexene

[1125-99-1] **$C_{10}H_{17}N$**



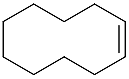
Benzenediazonium-2-carboxylate

See Benzenediazonium-2-carboxylate: 1-Pyrrolidinylcyclohexene

See related ALKENES

3345. *cis*-Cyclododecene

[2198-20-1] **$C_{10}H_{18}$**

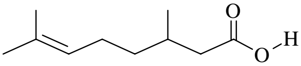


Preparative hazard

See Hydrazine: Metal salts (reference 3)

See other ALKENES

3346. Citronellic acid (3,7-Dimethyl-6-hexenoic acid)
[502-47-6] **$C_{10}H_{18}O_2$**

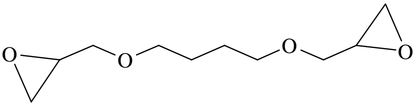


Ozone

See Ozone: Citronellic acid

See other ORGANIC ACIDS

3347. 1,4-Bis(2,3-epoxypropoxy)butane
[2425-79-8] **$C_{10}H_{18}O_4$**

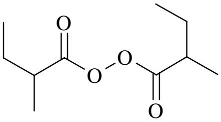


Trichloroethylene

See Trichloroethylene: Epoxides

See other 1,2-EPOXIDES

3348. Di-2-methylbutyryl peroxide
[1607-30-3] **$C_{10}H_{18}O_4$**

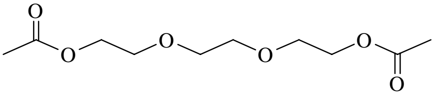


Swern, 1971, Vol. 2, 815

Pure material explodes on standing at ambient temperature.

See other DIACYL PEROXIDES

3349. 1,2-Bis(acetoxyethoxy)ethane (Triethylene glycol diacetate)
[111-21-7] **$C_{10}H_{18}O_6$**



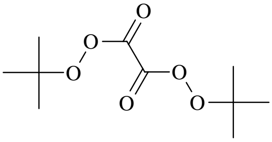
Acetic acid

Kolodner, H. J. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 345—355, Basle, SSCI, 1980

When fractional distillation at 150°C/27 mbar of a mixture of the ester with acetic acid (36% mol) was interrupted by admission of air, smoking and gas evolution occurred. This was attributed to cool flame auto-ignition and detailed investigation

confirmed this. Nitrogen should always be used to break vacuum, and further precautions are recommended.
See 2-Ethoxyethyl acetate
See COOL FLAMES

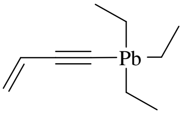
3350. *tert*-Butyl diperoxyoxalate
[14666-77-4] **$C_{10}H_{18}O_6$**



1. Castrantas, 1965, 17
2. Nutter, D. E. *et al., Chem. Abs.*, 1997, **126**, 263799v

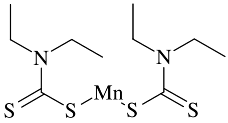
It exploded on removal from a freezing mixture [1]. Now attracts warnings as 'highly explosive' [2].
See other PEROXYESTERS

3351. 3-Buten-1-ynyltriethyllead
[30478-96-7] **$C_{10}H_{18}Pb$**



Zavagorodnii, S. V. *et al., Dokl. Akad. Nauk SSSR*, 1962, **143**, 855 (Engl. transl. 268)
It explodes on rapid heating.
See other ALKYLMETALS, METAL ACETYLIDES

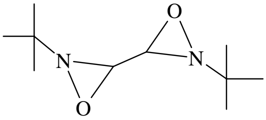
3352. Manganese(II) *N,N*-diethyldithiocarbamate
[15685-17-3] **$C_{10}H_{20}MnN_2S_4$**



Bailar, 1973, Vol. 3, 872
A pyrophoric solid.
See other PYROPHORIC MATERIALS

3353. 2,2'-Di-*tert*-butyl-3,3'-bioxaziridine

[54222-33-2] $C_{10}H_{20}N_2O_2$



Putnam, S. J. *et al., Chem. Eng. News*, 1958, **36**(23), 46

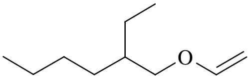
A sample prepared by an established method and stored overnight at 2°C exploded when disturbed with a metal spatula.

See 2,2''-Ethylenebis(3-phenyloxaziridine)

See other N—O COMPOUNDS, STRAINED-RING COMPOUNDS

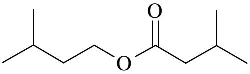
†3354. 2-Ethylhexyl vinyl ether

[103-44-6] $C_{10}H_{20}O$



†3355a. Isopentyl isovalerate

[659-70-1] $C_{10}H_{20}O_2$



3355b. 2-Dimethylaminomethylene-1,3-bis(dimethylimminio)propane diperchlorate

[2009-81-6] $Me_2NCH{=}C(CH{=}N^+Me_2)_2 2ClO_4^-$

$Me_2NCH{=}C(CH{=}N^+Me_2)_2 2ClO_4^-$

1. Ragan, J.A. *et al., Chem. Eng. News*, 2000, **78**(10), 8
2. Ragan, J.A. *et al., Synlett*, 2000, (8), 1172

This synthetic reagent is an explosive more powerful than TNT, and although relatively stable thermally, is very shock sensitive, exploding at impact < 7J. Replacement as a reagent by the equivalent, but far lower energy, tetrafluoroborate is recommended.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

3356. '10-Carbon oxime'

[ ] $C_{10}H_{21}NO$

Complex Structure

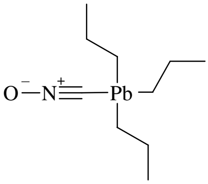
Knies, H., private comm., 1983

A 10-carbon oxime at 60°C was stored in an insulated container, and within 24 h the temperature had risen to 125°C, possibly owing to an exothermic Beckmann rearrangement to an amide. Application of cooling prevented a thermal runaway.

See other OXIMES

3357. Tripropyllead fulminate

[43135-83-7] **$C_{10}H_{21}NOPb$**



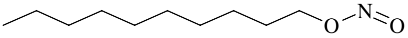
Houben-Weyl, 1975, Vol. 13.3, 101

An extremely explosive solid.

See related ALKYLMETALS, METAL FULMINATES

3358. Decyl nitrite

[1653-57-2] **$C_{10}H_{21}NO_2$**



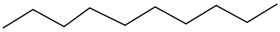
Hakl, J., *Runaway Reactions*, 1981, Paper 3/L, 4

Initial exothermic decomposition occurs at 115°C.

See other ALKYL NITRITES

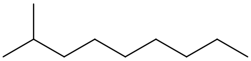
†3359. Decane

[124-18-5] **$C_{10}H_{22}$**



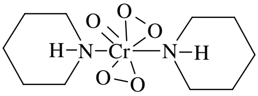
†3360. 2-Methylnonane

[34464-38-5] **$C_{10}H_{22}$**



3361. Oxodiperoxodipiperidinechromium(VI)

[ ] **$C_{10}H_{22}CrN_2O_5$**

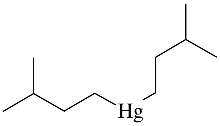


See Oxodiperoxodipyridinechromium(VI)

See other AMMINECHROMIUM PEROXOCOMPLEXES

3362. Diisopentylmercury

[24423-68-5] **$C_{10}H_{22}Hg$**



Iodine

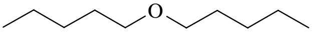
Whitmore, 1921, 103

Interaction is violent, accompanied by hissing.

See other ALKYLMETALS, MERCURY COMPOUNDS

†3363. Dipentyl ether

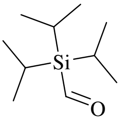
[693-65-2] **$C_{10}H_{22}O$**



HCS 1980, 719

3364. Formyl(triisopropyl)silane

[ ] **$C_{10}H_{22}OSi$**

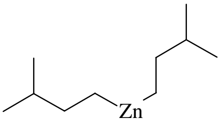


Soderquist, J. A. *et al., J. Amer. Chem. Soc.*, 1992, **114**(25), 10078

Pyrophoric.

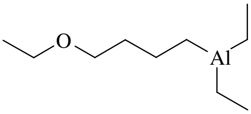
See other ALKYLSILANES

3365. Diisopentylzinc
[21261-07-4] **$C_{10}H_{22}Zn$**



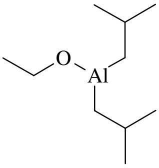
Gibson, 1969, 181
It ignites in air.
See other ALKYLMETALS, DIALKYLZINCS

3366. 4-Ethoxybutyldiethylaluminium
[65235-78-1] **$C_{10}H_{23}Al$**



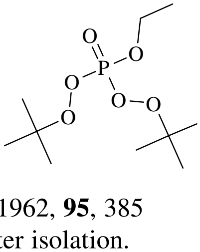
Bahr, G. *et al., Chem. Ber.*, 1955, **88**, 256
It ignites in air.
See related ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

3367. Ethoxydiisobutylaluminium
[15769-72-9] **$C_{10}H_{23}AlO$**



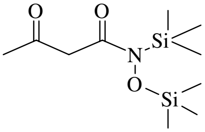
May ignite in air.
See entry ALKYLALUMINIUM ALKOXIDES AND HYDRIDES

3368. Di(*O—O-tert*-butyl) ethyl diperoxophosphate
[ ] **$C_{10}H_{23}O_6P$**



Rieche, A. *et al., Chem. Ber.*, 1962, **95**, 385
The liquid deflagrated soon after isolation.
See other TERT-BUTYL PEROXOPHOSPHATE DERIVATIVES, PHOSPHORUS ESTERS

3369. *N*-Trimethylsilyl-*N*-trimethylsilyloxyacetoacetamide
[87318-59-0] **$C_{10}H_{23}NO_3Si_2$**



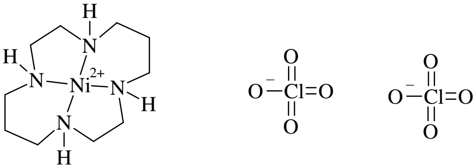
Oster, T. A. *et al., J. Org. Chem.*, 1983, **48**, 4309

It may decompose spontaneously if too high a distillation temperature is attained.

See other N—O COMPOUNDS

See related ALKYLSILANES

3370. 1,4,8,11-Tetraazacyclotetradecanenickel(II) perchlorate
[15220-72-1] **$C_{10}H_{24}Cl_2N_4Ni_2O_8$**



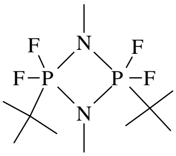
Barefield, E. K., *Inorg. Chem.*, 1972, **11**, 2274

It exploded violently during analytical combustion.

See TETRAAZAMACROCYCLANEMETAL PERCHLORATES

See other AMMINEMETAL OXOSALTS

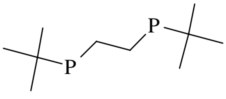
3371. 2,4-Di-*tert*-butyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine
[58656-11-4] **$C_{10}H_{24}F_4N_2P_2$**



Preparative hazard

See Butyllithium: 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine

3372. 1,2-Bis(*tert*-butylphosphino)ethane
[ ] **$C_{10}H_{24}P_2$**



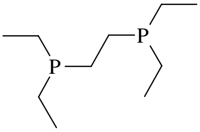
Benn, R. *et al., Z. Naturforsch. B*, 1987, **41B**, 680—691

The title compound and the bis(diisopropylphosphino) homologue were pyrophoric in air.

See related ALKYLPHOSPHINES

3373. 1,2-Bis(diethylphosphino)ethane

[6411-21-8] **$C_{10}H_{24}P_2$**



Mays. M. J. *et al., Inorg. Synth.*, 1974, **15**, 2

It ignites in air.

See other ALKYLPHOSPHINES

3374. Potassium [8-(4-nitrophenylthio)undecahydrodicarbaundecaborato]undecahydrodicarbaundecaboratocobaltate(1-) (Potassium [(7,8,9,10,11-η)-1,2,3,4,5, 6,7,8,9,11-decahydro-10-(4-nitrobenzenethiolato-*S*)-7,8-dicarbaundecaborato (2-)][(7,8,9,10,11-η)undecahydro-7,8-dicarbadecaborato(2-)cobaltate(1-))

[155147-43-6] **$C_{10}H_{25}B_{18}CoKNO_2S$**

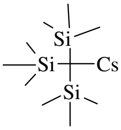
$[O_2NC_6H_4SC_2B_9H_{10}CoC_2B_9H_{11}]^- K^+$

See Potassium bis(8-(4-nitrophenylthio)undecahydrodicarbaundecaborato)cobaltate(1-)

See other BORANES

3375. Tris(trimethylsilyl)methylcaesium

[165610-13-9] **$C_{10}H_{27}CsSi_3$**



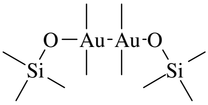
Eaborn, C. *et al., Angewand. Chem. (Int.)*, 1995, **34**(6), 687

This compound was isolated with 3.5 benzenes of crystallisation as moisture sensitive, pyrophoric, yellow plates.

See other ORGANOMETALLICS

3376. Tetramethylbis(trimethysilanoxy)digold

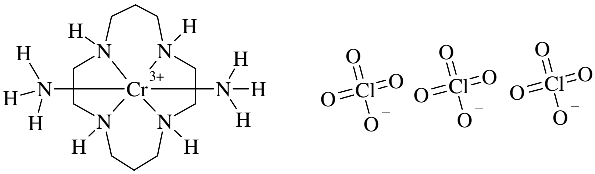
[15529-45-0] **$C_{10}H_{30}Au_2O_2Si_2$**



Schmidbaur, H. *et al., Inorg. Chem.*, 1966, **5**, 2069
Sublimed crystals decomposed explosively at 120°C.
See other GOLD COMPOUNDS
See related ALKYLMETALS

3377. *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) perchlorate

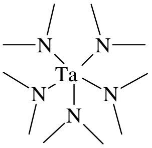
[94484-09-0] **$C_{10}H_{30}Cl_3CrN_6O_{12}$**



Kane-Maguire, N. A. P. *et al., Inorg. Chem.*, 1985, **24**, 597—605
It exploded on heating. Hexafluorophosphate is suggested as a more stable anion for this type of salt.
See other AMMINEMETAL OXOSALTS

3378. Pentakis(dimethylamino)tantalum

[ ] **$C_{10}H_{30}N_5Ta$**

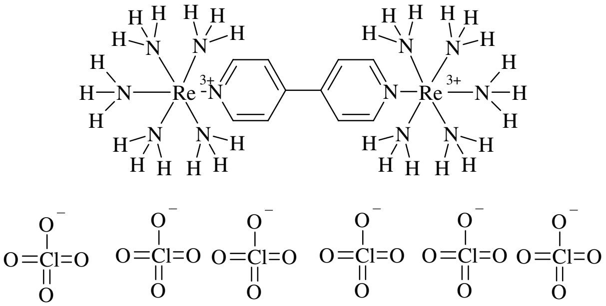


Preparative hazard

Chestnut, R. W. *et al., Chem. Eng. News*, 1990, **68**(31), 2
Preparation by reaction of tantalum pentachloride with pure lithium dimethylamide in pentane is unsafe. Initial non-reaction is followed by explosion during manipulation of the slurry. Presence of ether or dimethylamine gives smooth reaction. Stepwise displacement of chlorine, starting with the free amine, is also recommended.
See other N-METAL DERIVATIVES

3379. 4,4′-Bipyridyl-bis(pentaammineruthenium(III) perchlorate)

[69042-75-7] **$C_{10}H_{38}Cl_6N_{12}O_{24}Ru_2$**



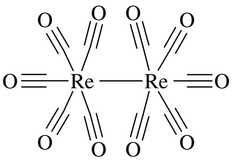
Sutton, J. E. *et al., Inorg. Chem.*, 1979, **18**, 1018

Use of the perchlorate salt gives a cleaner product than the tosylate, but is more hazardous.

See other AMMINEMETAL OXOSALTS

3380. Decacarbonyldirhenium

[14285-68-8] **$C_{10}O_{10}Re_2$**



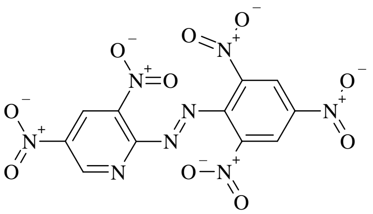
Bailar, 1973, Vol. 3, 953

It tends to ignite in air above 140°C.

See other CARBONYLMETALS

3381a. 3,5-Dinitro-2-(picrylazo)pyridine

[55106-93-9] **$C_{11}H_4N_8O_{10}$**



Explosive.

See entry POLYNITROAZOPYRIDINES

3381b. 1,3-Di(auroethynyl)-5-methylbenzene ([(5-Methyl-1,3-phenylene) di-2,1-ethynediyl]digold)

[273734-47-7] **$C_{11}H_6Au_2$**

$(AuC{\equiv}C)_2C_6H_3Me$

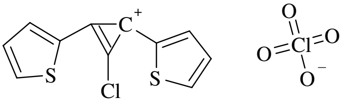
MacDonald, M-A. *et al., Organometallics*, 2000, **19**(11), 2194

This dialkyne metal salt, which exists in associated form, is shock sensitive.

See other METAL ACETYLIDES

3382. 1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate

[ ] **$C_{11}H_6Cl_2O_4S_2$**



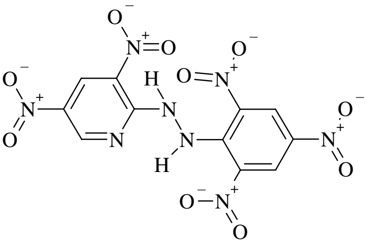
Komitsu, K. *et al., Tetrahedron Lett.*, 1978, 806

When isolated and dried, a violent explosion occurred. The tetrachloroaluminate salt is safer.

See other NON-METAL PERCHLORATES, STRAINED-RING COMPOUNDS

3383. 1-(3,5-Dinitro-2-pyridyl)-2-picrylhydrazine

[55106-92-8] **$C_{11}H_6N_8O_{10}$**

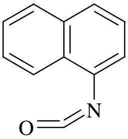


Explosive.

See entry POLYNITROAZOPYRIDINES

3384. 1-Naphthyl isocyanate

[1984-04-9] **$C_{11}H_7NO$**

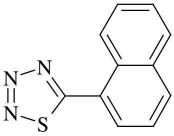


Energy of decomposition (in range 250—380°C) measured as 0.31 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

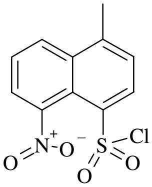
See other ORGANIC ISOCYANATES

3385a. (1-Napththyl)-1,2,3,4-thiatriazole
[95322-62-6] $C_{11}H_7N_3S$



CHETAH, 1990, 182
Shock sensitive.
See other N—S COMPOUNDS

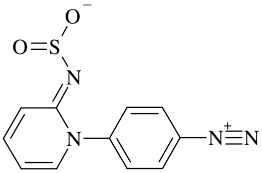
3385b. 4-Methyl-8-nitronaphthalene-1-sulfonyl chloride
[263153-09-9] $C_{11}H_8ClNO_4S$



1. Miller, R. A. *et al., J. Org. Chem.*, 2000, **65**(5), 1399
2. Editors comments

During safety testing of a pharmaceutical synthesis as part of scale-up, it was unexpectedly found that this not obviously unstable molecule is, in fact, shock sensitive, deflagrating modestly. It can also show thermal runaway from an initial temperature as low as 42°C. Maximum temperature rise rate of 380°C/min, pressure 340 Bar/min [1]. It will be remarked that the nitro and sulfonyl group can interact, and the resultant charged heterocycle may then lose a proton from the methyl group to give the equivalent of an *aci*-nitro group [2].
See other aci-NITROQUINONOID COMPOUNDS, NITROARYL COMPOUNDS

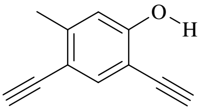
3386. 1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate
[61224-59-7] $C_{11}H_8N_4O_2S$



Hoffmann, H. *et al.*, US Pat. 3 985 724, 1977
Diazotisation of 2-*p*-aminophenylsulfonamidopyridine with subsequent adjustment of pH to 3—6 gives the internal diazonium salt, which decomposes violently at 230°C.
See other DIAZONIUM SALTS, N—S COMPOUNDS
See related DIAZONIUM CARBOXYLATES

3387a. 2,4-Diethynyl-5-methylphenol

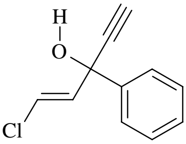
[32229-04-2] **$C_{11}H_8O$**



Myasnikova, R. N. *et al., Izv. Akad. Nauk SSSR*, 1970, **11**, 2637
Oxidation of the phenol or its methyl or propyl ethers in pyridine gave insoluble polymers. Those of the ethers exploded on heating.
See other ACETYLENIC COMPOUNDS, POLYPEROXIDES

3387b. 1-Chloro-3.phenylpent-1-en-4-yn-3-ol

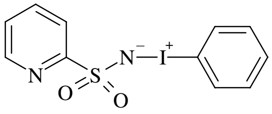
[33543-69-0] **$C_{11}H_9ClO$**



Acheson, R. M. *et al., J. Chem. Soc., Perkin Trans. 1*, 1987, 2322. 2326
In spite of very careful temperature control, explosive decomposition always occurred towards the end of vacuum distillation at 133—136°C/1 mbar.
See other ACETYLENIC COMPOUNDS, HALOACETYLENE DERIVATIVES

3387c. (2-Pyridylsulfonyliminoiodo)benzene ([(2-Pyridinylsulfonyl)aminophenyl] iodonium, inner salt)

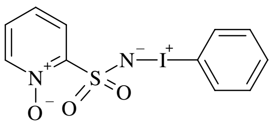
[243467-03-0] **$C_{11}H_9IN_2O_2S$**



See (ARYLSULFONYLIMINOIODO)BENZENES

3387d. (1-Oxopyrid-2-ylsulfonyliminoiodo)benzene ([(1-Oxo-2-pyridinylsulfonyl) aminophenyl]iodonium, inner salt)

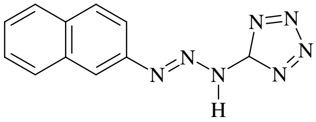
[243467-04-1] **$C_{11}H_9IN_2O_3S$**



See (ARYLSULFONYLIMINOIODO)BENZENES

3388a. 1-(2-Naphthyl)-3-(5-tetrazolyl)triazene

[68499-65-0] **$C_{11}H_9N_7$**



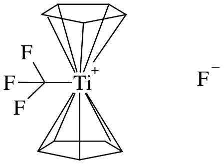
Thiele, J., *Ann.*, 1892, **270**, 54; 1893, **273**, 144

It explodes at 184°C.

See other TETRAZOLES, TRIAZENES

3388b. Dicyclopentadienyltrifluoromethyltitanium(1+) fluoride

[637039-91-9] **$C_{11}H_{10}F_4Ti$**



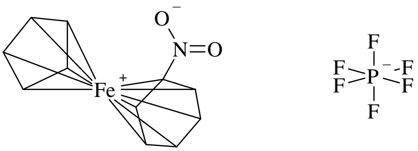
1. Taw, F. L. *et al., J. Amer. Chem. Soc.*, 2003, **125**(48), 14712
2. Taw, F. L. *et al., Chem. Abs.*, 2004, **140**, 42263c

Abstracted as liable to violent decomposition, the violence goes unmentioned in the primary source, as printed. The compound is there stated to decompose from around 20°C. The trifluoromethanesulfonate was also prepared and similarly unstable.

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3389. (Nitrobenzene)(cyclopentadienyl)iron(II) hexafluorophosphate

[77486-94-3] **$C_{11}H_{10}F_6FeNO_2P$**



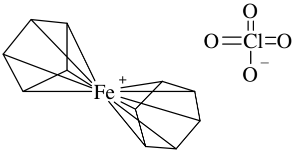
Gassman, P. G. *et al., Organometallics,* 1994, **13**(7), 2890

Heating this complex above 200°C may lead to explosion.

See other ORGANOMETALLICS

3390. η-Benzenecyclopentadienyliron(II) perchlorate

[ ] **$C_{11}H_{11}ClFeO_4$**



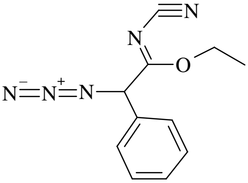
Denning, R. G. *et al., J. Organomet. Chem.*, 1966, **5**, 292

The dry material is shock-sensitive and detonated on touching with a spatula.

See other ORGANOMETALLIC PERCHLORATES

3391. Ethyl α-azido-*N*-cyanophenylacetimidate

[51688-25-6] **$C_{11}H_{11}N_5O$**



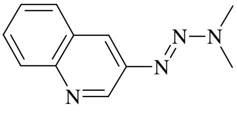
Petersen, H. J., *J. Med. Chem.*, 1974, **17**, 104

The crude imidoester should be used as a concentrated solution in ether. A small solvent-free sample exploded violently.

See related 2-AZIDOCARBONYL COMPOUNDS

3392a. 3,3-Dimethyl-1-(3-quinolyl)triazene

[70324-23-1] **$C_{11}H_{12}N_4$**



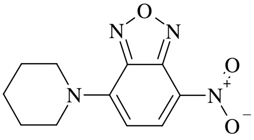
Rondevstedt, C. S. *et al., J. Org. Chem.*, 1957, **22**, 201

The crude material decomposes violently if allowed to dry, and purified material explodes at 131°C or during analytical combustion.

See other TRIAZENES

3392b. 4-Nitro-7-piperidino[1,2,5]benzoxadiazole (4-Nitro-7-piperidino[2,1,3] benzoxadiazole)

[18378-22-8] **$C_{11}H_{12}N_4O_3$**

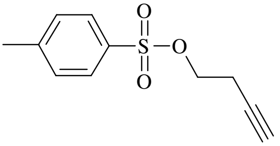


Boga, C. *et al., J. Chem. Soc., Perk. 2*, 2001, (8), 1408

The paper describes all its isolated products from reaction of nucleophiles with nitrobenzofuroxan as explosive. This, the final product of reaction with piperidine, will probably be the most stable of them.

3393. 3-Butyn-1-yl 4-toluenesulfonate

[23418-85-1] **$C_{11}H_{12}O_3S$**



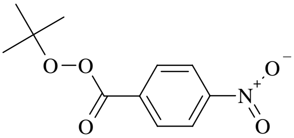
Eglinton, G. *et al., J. Chem. Soc.*, 1950, 3653

The material could be distilled in small amounts at below 0.01 mbar, but exploded on attempted distillation at 0.65 mbar.

See other ACETYLENIC COMPOUNDS, SULFUR ESTERS

3394. *tert*-Butyl 4-nitroperoxybenzoate

[16166-61-3] **$C_{11}H_{13}NO_5$**



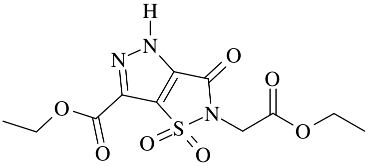
Criegee, R. *et al., Ann.*, 1948, **560**, 135

This and the 4-nitrobenzoates of homologous *tert*-alkyl hydroperoxides explode in contact with flame.

See other NITROARYL COMPOUNDS, PEROXYESTERS

3397a. Ethyl 6-ethoxycarbonyl-3,4-dihydro-1,1,3-trioxo-2-pyrazolo[3,4-d] isothiazole-2-acetate

[126623-77-6] **$C_{11}H_{13}N_3O_7S$**



Burri, K. F., *Helv. Chim. Acta*, 1989, **72**(6), 1416

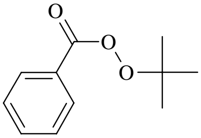
It is suggested that this compound, and two precursors, can explode.

See Ethyl 4-bromo-1,1,3-trioxoisothiazoleacetate

See other N—S COMPOUNDS

†3397b. *tert*-Butyl peroxybenzoate

[614-45-9] **$C_{11}H_{14}O_3$**



1. Criegee, R., *Angew. Chem.*, 1953, **65**, 398—399
2. Schnur, R. C., *Chem. Eng. News*, 1981, **59**(19), 3
3. Verhoeff, J., *Experimental Study of the Thermal Explosion of Liquids*, Doctoral thesis, University of Delft, 1983
4. *CHETAH*, 1990, 182

Shortly after interruption of vacuum distillation from an oil-bath at 115°C to change a thermometer, the ester exploded violently and this was attributed to overheating [1]. A commercial sample of undetermined age exploded violently just after vacuum distillation had begun [2]. In an examination of thermal explosion behaviour, the title compound was used as a model compound in autoclave experiments at low, high or constant pressure. Three stages in the overall process were identified: thermal runaway, initiation, and then explosion, and these are studied and discussed in detail. In the high pressure experiments, maximum rates of pressure rise approaching 1000 kbar/s were observed [3]. It is shock sensitive [4].

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Copper(I) bromide, Limonene

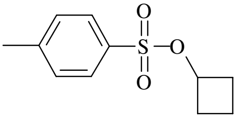
Wilson, C. W. *et al., J. Agric. Food Chem.*, 1975, **23**, 636

Addition of all the perester in one portion to limonene and catalytic amounts of copper(I) bromide before oxidation had begun, as shown by development of a blue-green colour, led to an explosion.

See other PEROXYESTERS

3398a. Cyclobutyl 4-methylbenzenesulfonate

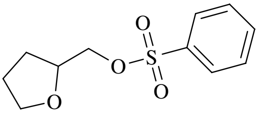
[10437-85-1] **$C_{11}H_{14}O_3S$**



It decomposes vigorously at 118°C.
See entry SULFONIC ACID ESTERS
See other SULFUR ESTERS

3398b. Tetrahydrofurfuryl benzenesulfonate

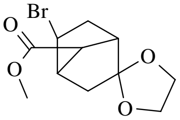
[100059-56-1] **$C_{11}H_{14}O_4S$**



Bruneton, C. *et al., Computers Chem. Engng.*, 1997, 21, S311
This molecule is unstable, with incredibly high maximum rates of temperature and pressure rise calorimetrically determined (14,000°C and 1,500 bar per min) even though dissolved in a solvent. Several pages of computerised fantasy over the heat of decomposition, based solely on identified, but unquantified, volatiles while neglecting the black tar which is probably the major product, leave readers no wiser as to the circumstances. The original reactor-burst during manufacture from the alcohol and the sulfonyl chloride in the unspecified solvent should have started at around room temperature; this formation reaction is presumably exothermic. The usual solvents for such reactions, tertiary amines, would also be important reagents in decomposition chemistry.
See other SULFUR ESTERS

3399. Methyl spiro[5-bromobicyclo[2.2.1]heptane 2,2' 1,3-dioxolane]-7-carboxylate

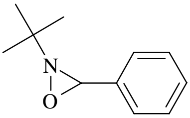
[71155-12-9] **$C_{11}H_{15}BrO_4$**



Perchloryl fluoride
See Perchloryl fluoride: Methyl 2-bromo-5,5-(ethylenedioxy)[2.2.1]bicycloheptane-7-carboxylate

3400. 2-*tert*-Butyl-3-phenyloxaziridine

[7731-34-2] **$C_{11}H_{15}NO$**



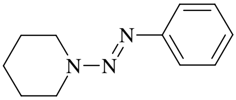
Emmons, W. D. *et al., Org. Synth.*, 1969, **49**, 13

Vacuum distillation of this active oxygen compound is potentially hazardous and precautions are necessary.

See other N—O COMPOUNDS, STRAINED-RING COMPOUNDS

3401. *N*-Phenylazopiperidine

[16978-76-0] **$C_{11}H_{15}N_3$**



Hydrofluoric acid

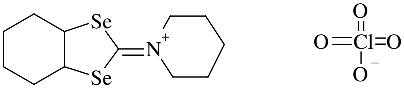
Wallach, O. *et al., Ann.*, 1886, **235**, 258; 1888, **243**, 219

Interaction to give fluorobenzene is violent and is not suitable for above 10 g quantities.

See other TRIAZENES

3402. 2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate

[76371-73-8] **$C_{11}H_{16}ClNO_4Se_2$**

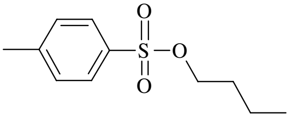


See entry 1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES

See other PERCHLORATE SALTS OF NITROGENOUS BASES

3403. Butyl toluenesulfonate (Butyl 4-methylbenzenesulfonate)

[778-28-9] **$C_{11}H_{16}O_3S$**



Boyer, J. H. *et al., J. Org. Chem.* 1958, **23**, 1051

Eight grams of the crude ester, which had been prepared from tosyl azide and sodium butoxide, then stored for four weeks at 0°C, was to be distilled at 0.2 mm Hg. On the bath reaching 70°C, there was a violent explosion. This was attributed to a toluenesulphonic acid autocatalysed elimination. However, presence of butyl azide as an impurity seems probable.

See also AZIDES
See other SULFONIC ACID ESTERS

3404. Oxodiperoxy(pyridine)(1,3-dimethyl-2,4,5,6-tetrahydro-2-1*H*)-(pyrimidinone) molybdenum

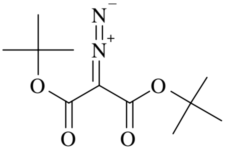
[128575-71-3] **$C_{11}H_{17}MoN_3O_6$**

Complex structure

Preparative hazard
See Oxodiperoxy(1,3-dimethyl-2,4,5,6-tetrahydro-2-1*H*)-(pyrimidinone) molybdenum
See related AMMINECHROMIUMPEROXO COMPLEXES

3405. Di-*tert*-butyl diazomalonate

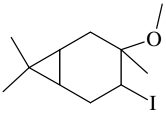
[35207-75-1] **$C_{11}H_{18}N_2O_4$**



Ledon, H. J., *Org. Synth.*, 1979, **59**, 70
Although no explosions have been encountered during the distillation of 10 g portions under argon at 54—58°C/0.003 mbar, it should be treated as potentially explosive. Contact with rough or metallic surfaces should be avoided.
See other DIAZO COMPOUNDS

3406a. 3-Iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0]heptane

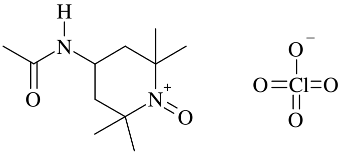
[65082-64-6] **$C_{11}H_{19}IO$**



See vic-IODO-ALKOXY COMPOUNDS
See other IODINE COMPOUNDS

3406b. 4-Acetylamino-1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate (4-Acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate)

[219543-08-5] **$C_{11}H_{20}ClN_2O_6$**

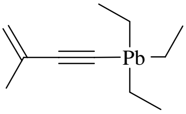


Bobbitt, J, M., *Chem. Eng. News*, 1999, **77**(29), 6

This organic oxidant, initially claimed a safe reagent, later showed the treacherous explosibility normal to organic perchlorates. The far less hazardous tetrafluoroborate is an equally effective reagent.
See other N—O COMPOUNDS, PERCHLORATES

3407. 3-Methyl-3-buten-1-ynyltriethyllead

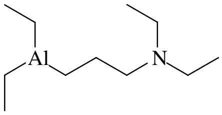
[ ] **$C_{11}H_{20}Pb$**



Zavgorodnii, S. V. *et al., Doklad. Akad. Nauk SSSR*, 1962, **143**, 855 (Engl. transl. 268)
It explodes on rapid heating.
See other ALKYLMETALS, METAL ACETYLIDES

3408. Diethyl-3-diethylaminopropylaluminium

[73506-71-5] **$C_{11}H_{26}AlN$**

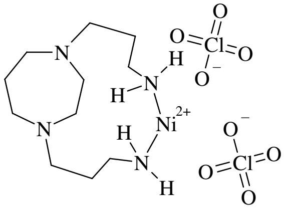


491M, 19758, 151

It ignites in air.
See related TRIALKYLALUMINIUMS

3409. *N,N*-Bis(3-aminopropyl)-1,4-diazacycloheptanenickel(II) perchlorate

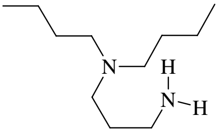
[70212-12-3] **$C_{11}H_{26}Cl_2N_4NiO_8$**



Billo, E. J., *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 502
An explosive solid.
See other AMMINEMETAL OXOSALTS

3410. 3-Dibutylaminopropylamine

[30734-83-9] **$C_{11}H_{26}N_2$**



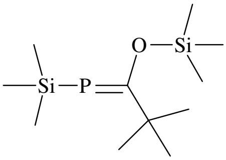
Cellulose nitrate

See CELLULOSE NITRATE: Amines

See other ORGANIC BASES

3411. 1-Trimethylsilyloxy-1-trimethylsilylphosphylidine-2,2-dimethylpropane (4-(Dimethylethyl)-2,2,6,6-tetramethyl-3-oxa-5-phospha-2,6-disilahept-4-ene)

[78114-26-8] **$C_{11}H_{27}OPSi_2$**



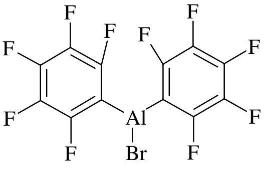
Becker, G. *et al., Inorg. Synth.*, 1990, **27**, 249

Extremely oxygen sensitive and pyrophoric.

See other ALKYLPHOSPHINES

3412. Bis(pentafluorophenyl)aluminium bromide

[4457-91-4] **$C_{12}AlBrF_{10}$**



Air, or Ether, or Water

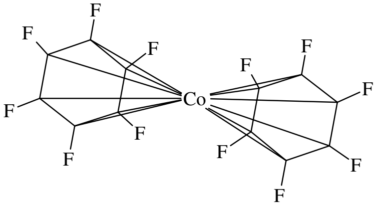
1. Chambers, R. D. *et al., J. Chem. Soc. (C)*, 1967, 2185
2. Chambers, R. D. *et al., Tetrahedron Lett.*, 1965, 2389
3. Cohen, C. S. *et al., Advan. Fluorine Chem.*, 1970, **6**, 156

It ignites in air, explodes during uncontrolled hydrolysis [1], and chars during controlled hydrolysis [2]. When isolated as the etherate, attempts to remove solvent ether caused violent decomposition [3].

See other HALO-ARYLMETALS

3413. Bis(hexafluorobenzene)cobalt(0)

[ ] **$C_{12}CoF_{12}$**

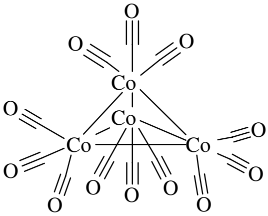


It decomposes explosively at 10°C

See entry HALOARENEMETAL π-COMPLEXES

3414. Dodecacarbonyltetracobalt

[19212-11-4] **$C_{12}Co_4O_{12}$**



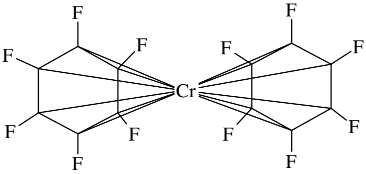
Blake, E. J., private comm., 1974

Cobalt catalysts discharged from ‘oxo’-process reactors are frequently pyrophoric, owing to the presence of the carbonylcobalt.

See other CARBONYLMETALS, PYROPHORIC CATALYSTS

3415. Bis(hexafluorobenzene)chromium(0)

[59420-01-8] **$C_{12}CrF_{12}$**



It decomposes explosively at 40°C.

See entry HALOARENEMETAL π-COMPLEXES

3416a. Graphite hexafluorogermanate

[79270-41-0] **$C_{12}F_6Ge$**

$C_{12}GeF_6$

McCarron, E. M. *et al., J. Chem. Soc., Chem. Comm.*, 1980, 890—891

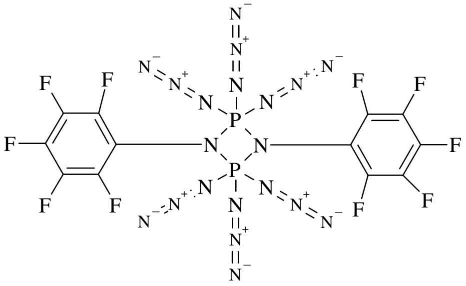
The solid product of intercalating graphite with germanium tetrafluoride—fluorine mixtures at 20°C is thought to have an oxidising and fluorinating capability close to that of elemental fluorine itself.

See Fluorine

See other OXIDANTS

3416b. 1,3-Di(pentafluorophenyl)-2,2,2,4,4,4-hexaazido-1,3-diaza-2,4-diphosphetidine

[389868-02-4] **$C_{12}F_{10}N_{20}P_2$**



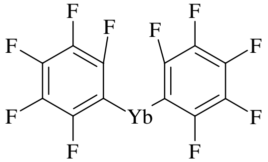
Aubauer, C. *et al., Zeitschrift für Anorg. & Allgem. Chem.*, 2001, **627**(11), 2547

It exploded on melting (80°C)

See other NON-METAL AZIDES

3417. Bis(pentafluorophenyl)ytterbium

[66080-22-6] **$C_{12}F_{10}Yb$**



Methylcyclopentadiene

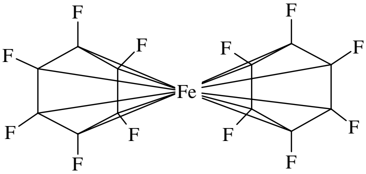
Deacon, G. B. *et al., Aust. J. Chem.*, 1985, **38**, 1763

The THF-solvated product of the ligand exchange reaction between bis(pentafluorophenyl)ytterbium and methylcyclopentadiene was explosive. The expected product, bis(methylcyclopentadiene)ytterbium, obtained by another exchange route, is not explosive.

See other ORGANOMETALLICS

3418. Bis(hexafluorobenzene)iron(0)

[37279-26-8] **$C_{12}F_{12}Fe$**

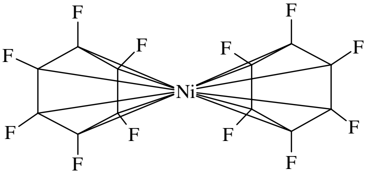


It decomposes explosively at —40°C.

See entry HALOARENEMETAL π-COMPLEXES

3419. Bis(hexafluorobenzene)nickel(0)

[74167-05-8] **$C_{12}F_{12}Ni$**



Alone, or Air, or Hydrogen, or Carbon monoxide, or Allyl bromide, or Trifluoromethyl iodide

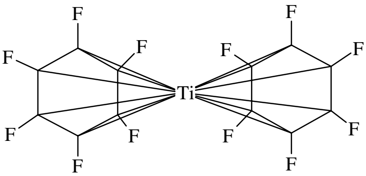
Klabunde, K. J. *et al., J. Fluorine Chem.*, 1974, **4**, 114—115

The complex decomposes explosively on slight provocation (flakes falling into the reactor, static charge or uneven warming) and at 70°C with careful heating. At ambient temperature, interaction with air or the reagents above is explosive, but can be controlled by preliminary cooling to —196°C, followed by controlled slow warming.

See entry HALOARENEMETAL π-COMPLEXES

3420. Bis(hexafluorobenzene)titanium(0)

[ ] **$C_{12}F_{12}Ti$**

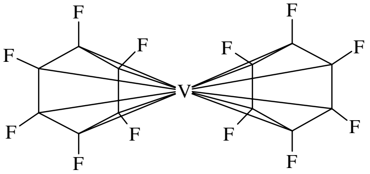


It decomposes explosively at —50°C.

See entry HALOARENEMETAL π-COMPLEXES

3421. Bis(hexafluorobenzene)vanadium(0)

[ ] **$C_{12}F_{12}V$**

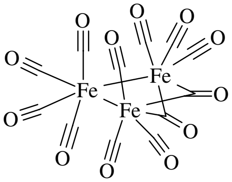


It decomposes explosively at 100°C.

See entry HALOARENEMETAL π-COMPLEXES

3422a. Dodecacarbonyltriiron

[17685-52-8] [100447-70-9] **$C_{12}Fe_3O_{12}$**



King, R. B. *et al., Inorg. Synth.*, 1963, **7**, 195

On prolonged storage, pyrophoric decomposition products are formed.

See other CARBONYLMETALS

3422b. 2,3,4,5,6,7,8,9,10,11-Deca(trifluoromethyl)-1,12-dicarbadodecaborane

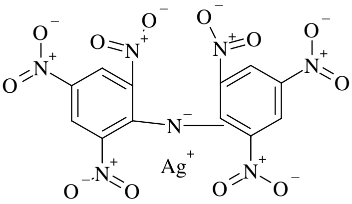
[356060-62-3] **$C_{12}H_2B_{10}F_{30}$**

Complex structure

2,3,4,5,6,7,8,9,10,11-Decamethyl-1,12-dicarbadodecaborane

3423. Silver hexanitrodiphenylamide

[32817-38-2] (ion) **$C_{12}H_4AgN_7O_{12}$**



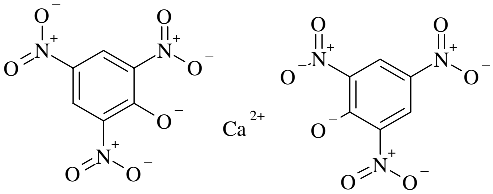
Taylor, C. A. *et al., Army Ordnance*, 1926, **7**, 68—69

It had been evaluated as a detonator.

See other N-METAL DERIVATIVES, POLYNITROARYL COMPOUNDS, SILVER COMPOUNDS

3424. Calcium picrate

[16824-78-5] **$C_{12}H_4CaN_6O_{14}$**

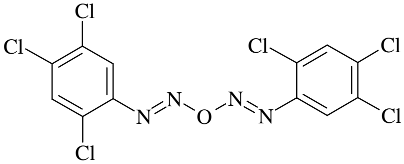


See Picric acid (reference 3)

See other PICRATES, POLYNITROARYL COMPOUNDS

3425. Bis(2,4,5-trichlorobenzenediazo) oxide

[ ] **$C_{12}H_4Cl_6N_4O$**



Alone, or Benzene

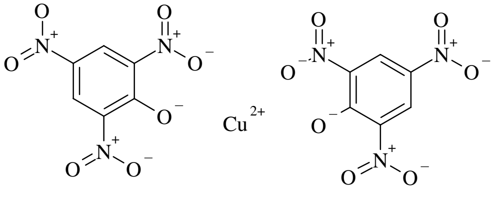
Kaufmann, T. *et al., Ann.*, 1960, **634**, 77

The dry solid explodes under a hammer-blow, or on moistening with benzene.

See other BIS(ARENEDIAZO) OXIDES, HALOARYL COMPOUNDS

3426. Copper(II) picrate

[33529-09-8] **$C_{12}H_4CuN_6O_{14}$**

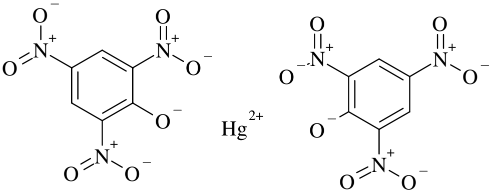


See Picric acid (reference 2)

See other PICRATES, POLYNITROARYL COMPOUNDS

3427. Mercury(II) picrate

[19528-48-4] **$C_{12}H_4HgN_6O_{14}$**

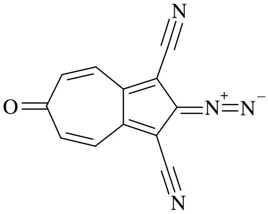


See Picric acid (reference 2)

See other MERCURY COMPOUNDS, PICRATES, POLYNITROARYL COMPOUNDS

3428. 1,3-Dicyano-2-diazo-2,6-azulene quinone (2-Diazo-2,6-dihydro-6-oxo-1.3-azulenedicarbonitrile)

[53535-47-0] **$C_{12}H_4N_4O$**



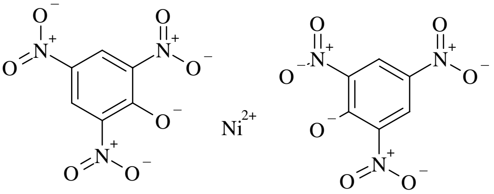
Nosoe, T. *et al., J. Org. Chem*,. 1995, **60**(18), 5919

The compound sometimes decomposes explosively at 155°C.

See other ARENEDIAZOMIUM OXIDES

3429. Nickel picrate

[63085-06-3] **$C_{12}H_4N_6NiO_{14}$**



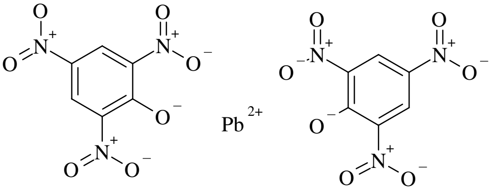
Bernardi, A., *Gazz. Chim. Ital.*, 1930, **60**, 169—171

It deflagrates or explodes very violently on heating.

See other HEAVY METAL DERIVATIVES, PICRATES, POLYNITROARYL COMPOUNDS

3430. Lead(II) picrate

[6477-64-1] **$C_{12}H_4N_6O_{14}Pb$**



Belcher, R., *J. R. Inst. Chem.*, 1960, **84**, 377

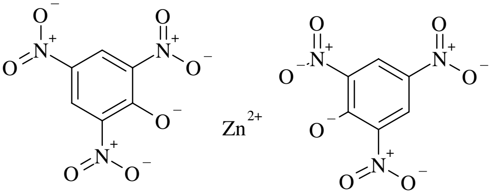
During the traditional qualitative inorganic analytical procedure, samples containing the lead and salicylate radicals can lead to the formation and possible detonation of lead picrate. This arises during evaporation of the filtrate with nitric acid, after precipitation of the copper—tin group metals with hydrogen sulfide. Salicylic acid is converted under these conditions to picric acid, which in presence of lead gives explosive lead picrate. An alternative (MAQA) scheme is described which avoids this possibility.

See Picric acid (reference 2)

See other HEAVY METAL DERIVATIVES, PICRATES, POLYNITROARYL COMPOUNDS

3431. Zinc picrate

[16824-81-0] **$C_{12}H_4N_6O_{14}Zn$**

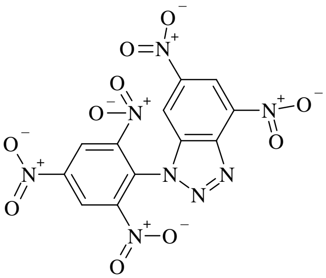


See Picric acid (reference 2)

See other PICRATES, POLYNITROARYL COMPOUNDS

3432. 4,6-Dinitro-1-picrylbenzotriazole

[50892-86-9] **$C_{12}H_4N_8O_{10}$**

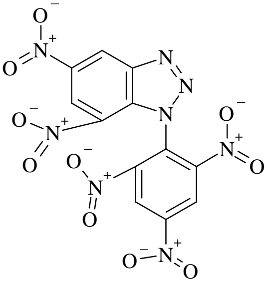


Coburn, M. D., *J. Heterocycl. Chem.*, 1973, **10**, 743—746

The isomeric dinitro derivatives, and some of the mononitro derivatives, are impact-sensitive explosives.

See other POLYNITROARYL COMPOUNDS, TRIAZOLES

3433. 5,7-Dinitro-1-picrylbenzotriazole
[50892-90-5] **$C_{12}H_4N_8O_{10}$**

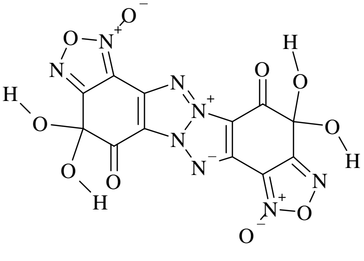


Coburn, M. D., *J. Heterocycl. Chem.*, 1973, **10**, 743—746

The isomeric dinitro derivatives, and some of the mononitro derivatives, are impact-sensitive explosives.

See other POLYNITROARYL COMPOUNDS, TRIAZOLES

3434. 5,12-Dioxo-4,4,11,11-tetrahydroxy-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3’,4’:4,5]benzotriazolo[2,1-*a*]benzotriazolo-*b*-ium 1,8-dioxide
[ ] **$C_{12}H_4N_8O_{10}$**



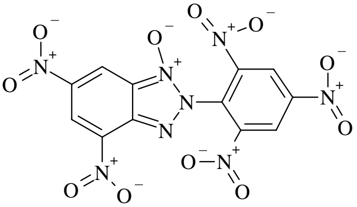
Subramanian, G. *et al., J. Org. Chem.*, 1996, **61**(5), 1898

This, and the tetraketone resulting from dehydration of the gem-diol groups, both explode under a hammer blow.

See other FURAZAN *N*-OXIDES

3435. 4,6-Dinitro-2-(2,4,6-trinitrophenyl)benzotriazole *N*-oxide

[87604-86-2] **$C_{12}H_4N_8O_{11}$**



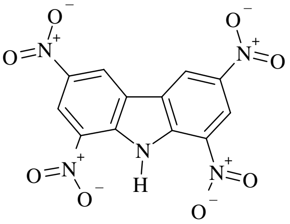
Renfrow, R. A. *et al., Aust. J. Chem.*, 1983, **36**, 1847

It is explosive and a super-electrophile, like 4,6-dinitrobenofurazan *N*-oxide.

See other N-OXIDES, POLYNITROARYL COMPOUNDS, TRIAZOLES

3436. 1,3,6,8-Tetranitrocarbazole

[4543-33-3] **$C_{12}H_5N_5O_8$**



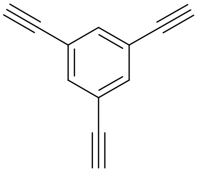
Sorbe, 1968, 153

It may readily explode when dry, so it should be stored wet with water (10% is normally added to commercial material).

See other POLYNITROARYL COMPOUNDS

3437. 1,3,5-Triethynylbenzene

[17814-74-3] **$C_{12}H_6$**



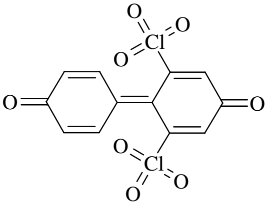
Shvartsberg, M. S. *et al., Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, **110**, 1836

It polymerised explosively on rapid heating and compression.

See other ACETYLENIC COMPOUNDS, POLYMERISATION INCIDENTS

3438. 2,6-Diperchloryl-4,4-diphenoquinone

[ ] **$C_{12}H_6Cl_2O_8$**



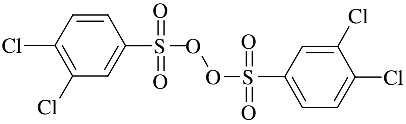
Gardner, D. M. *et al., J. Org. Chem.*, 1963, **28**, 2650

A shock-sensitive explosive.

See other PERCHLORYL COMPOUNDS

3439. Bis(3,4-dichlorobenzenesulfonyl) peroxide

[ ] **$C_{12}H_6Cl_4O_6S_2$**



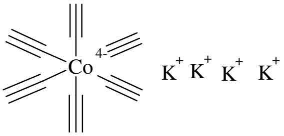
Dannley, R. *et al., J. Org. Chem.*, 1966, **31**, 154

The peroxide was too unstable to dry thoroughly; such samples often exploded spontaneously.

See other DIACYL PEROXIDES

3440. Potassium hexaethynylcobaltate(4—)

[ ] **$C_{12}H_6CoK_4$**



Alone, or Ammonia

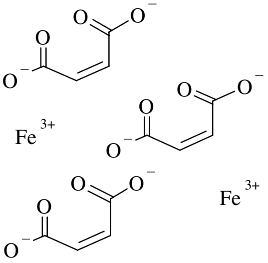
Nast, R. *et al., Z. Anorg. Chem.*, 1955, **282**, 210

It is moderately stable at below —30°C, is very shock- and friction-sensitive, and explodes violently on contact with water. At ambient temperature, it rapidly forms explosive decomposition products. Its addition compound with ammonia behaves similarly, exploding on contact with air.

See other COMPLEX ACETYLIDES

3441. Iron(III) maleate

[14451-00-4] **$C_{12}H_6Fe_2O_{12}$**



Iron(III) hydroxide

Thermally unstable basic iron(III) maleates produced from mixtures of the above may be pyrophoric.

See Phthalic anhydride (reference 2)

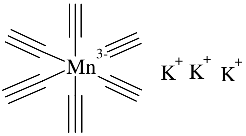
Sulfur compounds

See Phthalic anhydride (reference 2)

See other HEAVY METAL DERIVATIVES

3442. Potassium hexaethynylmanganate(3—)

[ ] **$C_{12}H_6K_3Mn$**



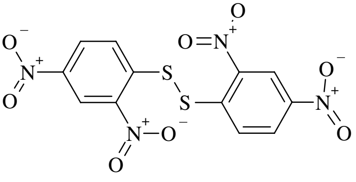
Bailar, 1973, Vol. 3, 855

A highly explosive solid.

See other COMPLEX ACETYLIDES

3443. Bis(2,4-dinitrophenyl) disulfide

[2217-55-2] **$C_{12}H_6N_4O_8S_2$**

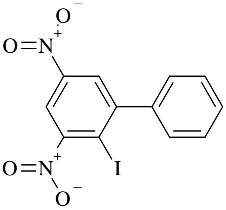


Chlorine

MCA Guide, 1972, 317

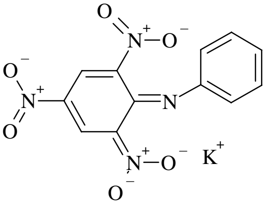
The disulfide was chlorinated in wet tetrachloroethylene to give dinitrobenzenesulfonyl chloride. When the solvent was being removed by evaporation, the residue exploded. Some of the less stable sulfenyl chloride may have been present.
See 2,4-Dinitrobenzenesulfenyl chloride
See other NON-METAL SULFIDES, POLYNITROARYL COMPOUNDS

3444. 2-Iodo-3,5-dinitrobiphenyl
[ ] **$C_{12}H_7IN_2O_4$**



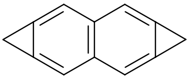
Ethyl sodioacetoacetate
Zaheer, S. H. *et al., J. Indian Chem. Soc.*, 1955, **32**, 491
Interaction of 2-halo-3,5-dinitrobiphenyls with the sodio ester should be limited to 5—6 g of the title compound to avoid explosions experienced with larger amounts.
See other HALOARYL COMPOUNDS, POLYNITROARYL COMPOUNDS

3445. Potassium 6-*aci*-nitro-2,4-dinitro-1-phenylimino-2,4-cyclohexadienide
[12245-12-4] (ion) **$C_{12}H_7KN_4O_6$**



Sudborough, J. J. *et al., J. Chem. Soc.*, 1906, **89T**, 586
The salt of the mono-*aci*-quinonoid form of 2,4,6-trinitrodiphenylamine is explosive, like the *N*-1- and -2-naphthyl analogues.
See other aci-NITROQUINONOID COMPOUNDS

3446. 1,4-Dihydrodicyclopropa[*b,g*]naphthalene
[52781-75-6] **$C_{12}H_8$**

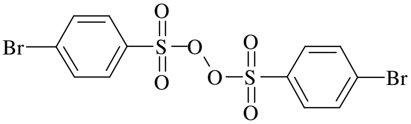


Ippen, J. *et al., Angew. Chem. (Intern. Ed.)*, 1974, **13**, 736

It undergoes explosive decomposition at 132—133°C, and is a shock-sensitive solid which requires handling with caution.

See other STRAINED-RING COMPOUNDS

3447. Bis(bromobenzenesulfonyl) peroxide
[29342-58-3] **$C_{12}H_8Br_2O_6S_2$**

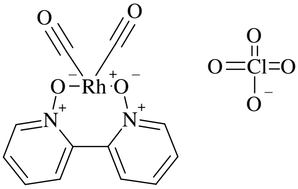


1. Bolte, J. *et al., Tetrahedron Lett.*, 1965, 1529
2. Dannley, R. L. *et al., J. Org. Chem.*, 1966, **31**, 154

The peroxide was too unstable to dry thoroughly; such samples often exploded spontaneously.

See other DIACYL PEROXIDES

3448. 2,2′-Bipyridine *N,N′*-dioxide-dicarbonylrhodium(I) perchlorate
[84578-88-1] **$C_{12}H_8ClN_2O_8Rh$**

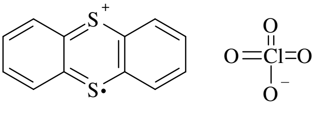


Uson, R. *et al., J. Organomet. Chem.*, 1982, **240**, 433 footnote f

It exploded violently during analytical combustion.

See related AMMINEMETAL OXOSALTS

3449. Thianthrenium perchlorate
[21299-20-7] **$C_{12}H_8ClO_4S_2$**



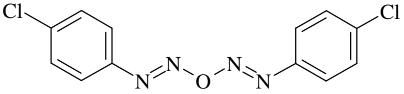
Shine, H. J. *et al., Chem. & Ind.*, 1969, 782; *J. Org. Chem.*, 1971, **36**, 2925

A 1—2 g portion of the freshly prepared suction-dried material exploded violently during transfer from a sintered filter. Initiation may have been caused by friction of transfer or rubbing with a glass rod. Preparation of 50—100 mg quantities only is recommended.

See other FRICTIONAL INITIATION INCIDENTS, NON-METAL PERCHLORATES

3450. Bis(4-chlorobenzenediazo) oxide

[ ] **$C_{12}H_8Cl_2N_4O$**



Alone, or Benzene

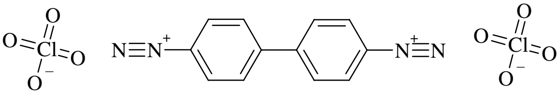
Bamberger, E., *Ber.*, 1896, **29**, 464

More stable than unsubstituted analogues, it may be desiccated at 0°C, but is then extremely sensitive and violently explosive. Contact with benzene (even at 0°C) is violent and the reaction may become explosive.

See other BIS(ARENEDIAZO) OXIDES, HALOARYL COMPOUNDS

3451. 4,4′-Biphenylenebis(diazonium) perchlorate (1,1′-Biphenyl-4,4′-bisdiazonium perchlorate)

[ ] **$C_{12}H_8Cl_2N_4O_8$**



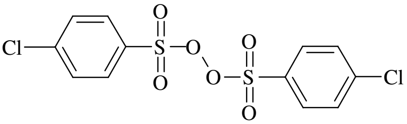
Vorlander, D., *Ber.*, 1906, **39**, 2713—2715

The perchlorate derived from tetrazotised benzidine is unstable and explosive.

See other DIAZONIUM PERCHLORATES

3452. Bis(4-chlorobenzenesulfonyl) peroxide

[1886-69-7] **$C_{12}H_8Cl_2O_6S_2$**



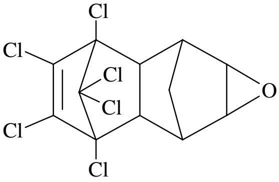
Dannley, R. L. *et al., J. Org. Chem.*, 1966, **31**, 154

The peroxide was too unstable to dry thoroughly; such samples often exploded spontaneously.

See other DIACYL PEROXIDES

3453. Endrin (1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo,endo-1,4:5,8-dimethanonaphthalene))

[72-20-8] **$C_{12}H_8Cl_6O$**



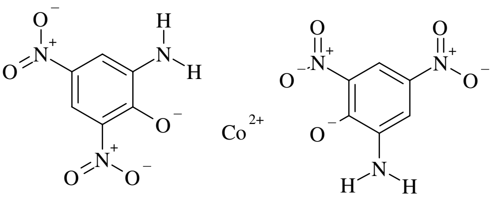
Diethyl 4-nitrophenyl thionophosphate

See Diethyl 4-nitrophenyl thionophosphate: Endrin

See other 1,2-EPOXIDES

3454. Cobalt(II) picramate

[33393-70-3] **$C_{12}H_8CoN_6O_{10}$**



Agrawal, J. P. *et al., Propellants, Explos.*, 1981, **6**, 112—116

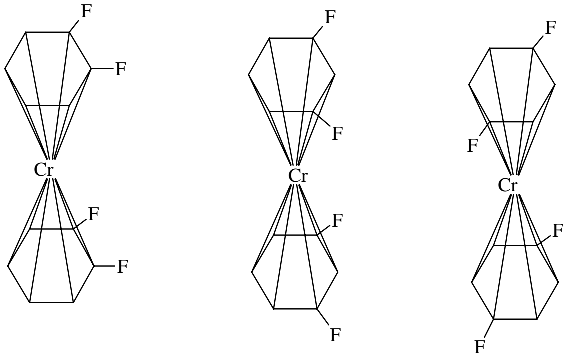
The picramate is less stable than the picrate.

See other HEAVY METAL DERIVATIVES, POLYNITROARYL COMPOUNDS

See related METAL NITROPHENOXIDES, PICRATES

3455. Bis(1,n-difluorobenzene)chromium(0) isomers

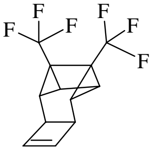
[53504-66-8] [53504-62-4] [39422-94-1] (1,2-, 1,3-, 1,4- resp.) **$C_{12}H_8CrF_4$**



All isomers unstable and explosive.

See entry HALOARENEMETAL π-COMPLEXES

3456. 3,6-Bis(trifluoromethyl)pentacyclo [6.2.0.0^{2,4}.0^{3,6}.0^{5,7}]dec-9-ene [24516-71-0] [96570-67-1] homopolymer $C_{12}H_8F_6$

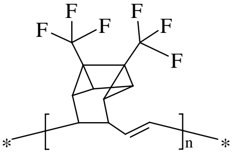


Editor's comments

The monomer is the highest energy stage of the Durham synthesis of polyacetylene; since the next stage, metathesized polymer, is known to be potentially explosive, the monomer is not likely to be absolutely safe.

See Poly(acetylene)

3457. Poly([7,8-bis(trifluoromethyl)tetracyclo [4.2.0.0^{2,8}.0^{5,7}]octane-3,4-diyl]-1,2-ethenediyl) [102868-70-2] $(C_{12}H_8F_6)_n$



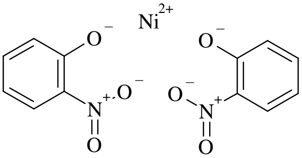
Feast, W. J., personal communication, 1993

This, the second stage of the Durham polyacetylene synthesis (and presumably identical to the homopolymer [96570-67-1]) is capable of explosion with one sixth the energy of TNT

See Poly(acetylene)

See other STRAINED-RING COMPOUNDS

3458. Nickel 2-nitrophenoxide hydrates: [54217-99-1], [54217-98-0] $C_{12}H_8N_2NiO_6$

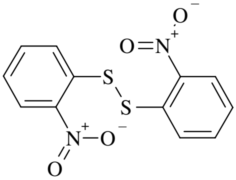


Bernardi, A., *Gazz. Chim. Ital.*, 1930, **60**, 166

It deflagrates violently or explodes on heating.

See other HEAVY METAL DERIVATIVES, METAL NITROPHENOXIDES, NITROARYL COMPOUNDS

3459. Bis(2-nitrophenyl) disulfide
[1115-00-6] **$C_{12}H_8N_2O_4S_2$**



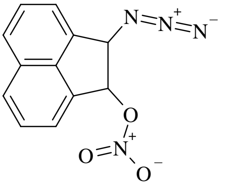
Anon., *Jahresber.*, 1977, 72—74

This is prepared from 2-nitrochlorobenzene and sodium disulfide in ethanol, and the reaction residue after recovery of the ethanol by steam distillation is known to be of limited thermal stability. On one occasion, a container (atypically with closed vents) of bulked residues totalling over 2 t exploded violently while awaiting collection for disposal. It seems remotely possible that an *aci*-nitro thioquinonimine species derived from 2-nitrobenzenethiol may have been involved.

See Sodium 2-nitrothiophenoxide

See other NON-METAL SULFIDES, POLYNITROARYL COMPOUNDS

3460. 2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate
[68026-59-5] **$C_{12}H_8N_4O_3$**

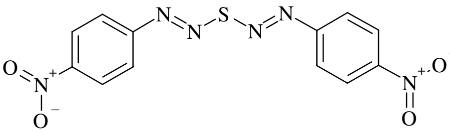


Trahanovsky, W. S. *et al., J. Amer. Chem. Soc.*, 1971, **93**, 5257

Although several other 1-azido-2-nitrato-alkanes appeared thermally stable, the acenaphthane derivative exploded violently on heating (probably during analytical combustion).

See other ALKYL NITRATES, ORGANIC AZIDES

3461a. Bis(4-nitrobenzenediazo) sulfide
[ ] **$C_{12}H_8N_6O_4S$**



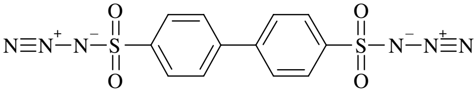
Tomlinson, W. R., *Chem. Eng. News*, 1951, **29**, 5473

The dry material is extremely sensitive and can be exploded by very light friction. It is too sensitive to handle other than as a solution, or as a dilute slurry in excess solvent, and then only on 1 g scale.

See other BIS(ARENEDIAZO) SULFIDES

3461b. 4,4′-Biphenylene-bis-sulfonylazide

[4712-19-0] **$C_{12}H_8N_6O_4S_2$**



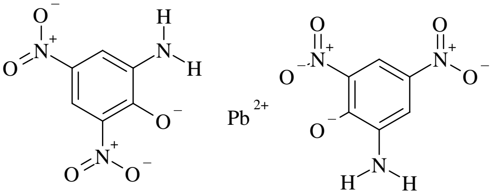
CHETAH, 1990, 182

Shock sensitive.

See other ACYL AZIDES

3462. Lead 2-amino-4,6-dinitrophenoxide

[111802-21-2] **$C_{12}H_8N_6O_{10}Pb$**



Sobela, B. *et al.*, Czech Pat. CS 245 822, 1987

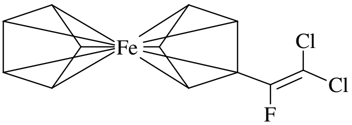
The lead salt is used as a minor component in compositions for low-power electric detonators.

See other HEAVY METAL DERIVATIVES, POLYNITROARYL COMPOUNDS

See related METAL NITROPHENOXIDES

3463. (2,2-Dichloro-1-fluorovinyl)ferrocene

[58281-24-6] **$C_{12}H_9Cl_2FFe$**



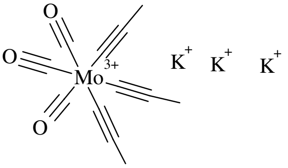
Okohura, K., *J. Org. Chem.*, 1976, **41**, 1493, footnote 14

Two attempts to purify the crude material by vacuum distillation led to sudden exothermic decomposition of the still contents. Distillation in steam was satisfactory.

See other ORGANOMETALLICS

See related HALOALKENES

3464. Potassium tricarbonyltris(propynyl)molybdate(3—)
[ ] **$C_{12}H_9K_3MoO_3$**

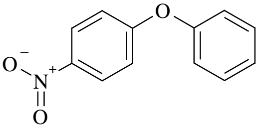


Houben-Weyl, 1975, Vol. 13.3, 470

It is pyrophoric.

See related CARBONYLMETALS, COMPLEX ACETYLIDES

3465. 4-Nitrodiphenyl ether
[2216-12-8] **$C_{12}H_9NO_3$**

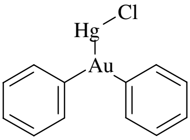


T_{ait24} was determined as 310°C by adiabatic Dewar tests, with an apparent energy of activation of 314 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other NITROARYL COMPOUNDS

3466. Chloromercuriodiphenylgold
[65381-02-4] **$C_{12}H_{10}AuClHg$**



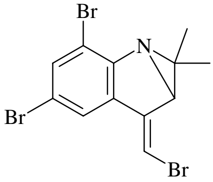
De Graaf, P. W. J. *et al., J. Organomet. Chem.*, 1977, **141**, 346

When dry it explodes violently, even at —20°C.

See other GOLD COMPOUNDS, MERCURY COMPOUNDS

3467. 3,5-Dibromo-7-bromomethylene-7,7a-dihydro-1,1-dimethyl-1*H*-azirino [1,2-a]indole

[34489-60-6] **$C_{12}H_{10}Br_3N$**



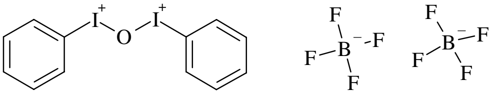
Brown, J. P., *et al., J. Chem. Soc. (C)*, 1971, 3631

A melting point sample exploded at 150°C. Larger quantities showed signs of autocatalytic decomposition from —30°C. This presumably involves release of strain in the aziridine ring.

See other STRAINED-RING COMPOUNDS

3468. Oxybisphenyliodonium bistetrafluoroborate

[119701-48-3] **$C_{12}H_{10}B_2F_8I_2O$**



1. van Look G., *Chem. Eng. News*, 1989 **67**(30), 2
2. Zhdankin, V. V. *et al., J. Org. Chem.,* 1989, **54,** 2607; 2609

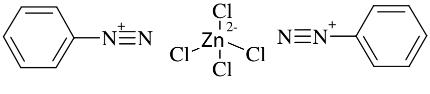
An explosion [1] of “iodosylbenzene tetrafluoroborate” attributed by *Chem. Abs*. to another structure is more likely to be of this, in view of the original synthetic papers [2].

See Iodosylbenzene tetrafluoroborate

See other IODINE COMPOUNDS

3469. Benzenediazonium tetrachlorozincate

[15727-43-2] **$C_{12}H_{10}Cl_4N_4Zn$**



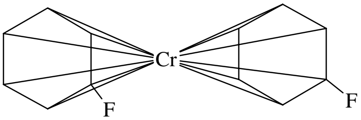
Muir, G. D., *Chem. & Ind.*, 1956, 58

A batch of the ‘double salt’ exploded, either spontaneously or from slight vibration, after thorough drying under vacuum at ambient temperature overnight. Although dry diazonium salts are known to be light-, heat- and shock-sensitive when dry, the double salts with zinc chloride were thought to be more stable. Presence of traces of solvent reduces the risk of frictional heating and deterioration.

See other DIAZONIUM SALTS

3470. Bis(fluorobenzene)chromium(0)

[42087-90-1] **$C_{12}H_{10}CrF_2$**

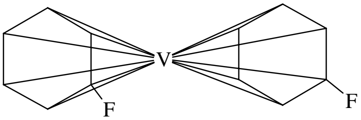


Unstable, potentially explosive

See entry HALOARENEMETAL π-COMPLEXES

3471. Bis(fluorobenzene)vanadium(0)

[53966-09-9] **$C_{12}H_{10}F_2V$**

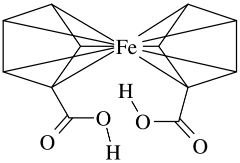


Unstable, potentially explosive.

See entry HALOARENEMETAL π-COMPLEXES

3472. Ferrocene-1,1′-dicarboxylic acid

[1293-87-4] **$C_{12}H_{10}FeO_4$**



Phosphoryl chloride

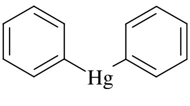
See Phosphoryl chloride: Ferrocene-1,1’-dicarboxylic acid

See other ORGANOMETALLICS

See related ORGANIC ACIDS

3473. Diphenylmercury

[587-85-9] **$C_{12}H_{10}Hg$**



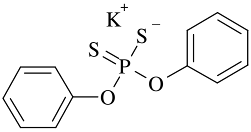
Chlorine monoxide, or Sulfur trioxide

1. Dreher, E. *et al., Ann.*, 1870, **154**, 127
2. Otto, R., *J. Prakt. Chem. [2]*, 1870, **1**, 183

Chlorine monoxide reacts violently [1], and sulfur trioxide very violently [2], with diphenylmercury.

See other ARYLMETALS, MERCURY COMPOUNDS

3475. Potassium *O,O*-diphenyl dithiophosphate
[3514-82-7] $C_{12}H_{10}KO_2PS_2$

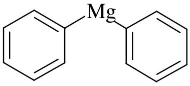


Arenediazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 10)

See related PHOSPHORUS ESTERS

3476. Diphenylmagnesium
[555-54-4] $C_{12}H_{10}Mg$



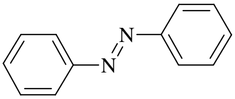
Air, or Carbon dioxide, or Water

1. Sidgwick, 1950, 234
2. Leleu, *Cahiers*, 1977, (88), 368

It ignites in moist (but not dry) air, reacts violently with water, reaching incandescence [1], and ignites in carbon dioxide [2].

See other ARYLMETALS, DIALKYLMAGNESIUMS

3477. Azobenzene (Diphenyldiazene)
[103-33-3] $C_{12}H_{10}N_2$



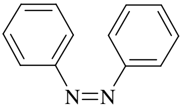
HCS 1980, 170

Heat of decomposition is determined as 0.80 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

See other AZO COMPOUNDS

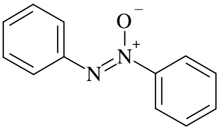
3478. *cis*-Azobenzene
[17082-12-1] $C_{12}H_{10}N_2$



Stull, 1977, 19

It is highly endothermic (ΔH_f° (s) +362.3 kJ/mol, 1.99 kJ/g). The *trans*-isomer [1080-16-6] will be less so.
See other ENDOTHERMIC COMPOUNDS

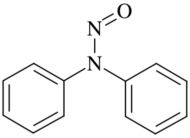
3479. Azoxybenzene
[495-48-7] **$C_{12}H_{10}N_2O$**



1. Stull, 1977, 18
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

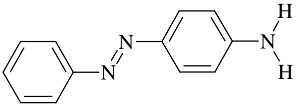
Azoxybenzene is moderately endothermic (ΔH_f° (s) +152.3 kJ/mol, 0.77 kJ/g). (The isolated stereoisomeric components [21650-65-7] '*cis*-', [20972-43-4] '*trans*-' may differ significantly from these values) [1]. Energy of decomposition in range 245—420°C measured by DSC as 1.303 kJ/g by DSC, and T_{ait24} was determined as 191°C by adiabatic Dewar tests, with an apparent energy of activation of 194 kJ/mol [2].
See other ENDOTHERMIC COMPOUNDS

3480. *N*-Nitrosodiphenylamine
[86-30-6] **$C_{12}H_{10}N_2O$**



Energy of decomposition (in range 300—500°C) measured as 0.65 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other NITROSO COMPOUNDS

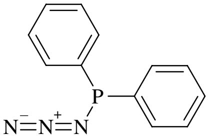
3481. 4-Aminophenylazobenzene
[60-09-3] **$C_{12}H_{11}N_3$**



Energy of decomposition (in range 145—365°C) measured as 0.522 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other AZO COMPOUNDS

3482. Diphenylphosphorus(III) azide

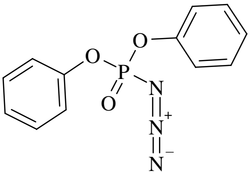
[4230-63-1] **$C_{12}H_{10}N_3P$**



Allcock, H. R. *et al., Macromolecules*, 1975, **8**, 380
The azide monomer, prepared in solution from the chlorophosphine and sodium azide, should not be isolated because it is potentially explosive.
See other NON-METAL AZIDES

3483. Diphenyl azidophosphate (Diphenyl phosphorazidate)

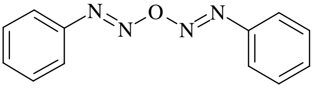
[26386-88-9] **$C_{12}H_{10}N_3O_3P$**



Nebuloni, M. *et al., J. Calorim., Anal. Therm. Thermodyn.*, 1986, **17**, 398—
Various methods were used to assess the thermal stability and potential hazards in handling the title compound.
See related NON-METAL AZIDES, PHOSPHORUS ESTERS

3484. Bis(benzeneazo) oxide

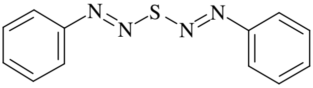
[ ] **$C_{12}H_{10}N_4O$**



Bamberger, E., *Ber.*, 1896, **29**, 460
Extremely unstable, it explodes on attempted isolation from the liquor, or on allowing the latter to warm to —18°C.
See other BIS(ARENEDIAZO) OXIDES

3485. Bis(benzenediazo) sulfide

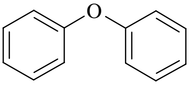
[22755-07-3] **$C_{12}H_{10}N_4S$**



Tomlinson, W. R., *Chem. Eng. News*, 1951, **29**, 5473

The wet solid can be exploded by impact or heating, and explodes while handling in air at ambient temperature. The material is too sensitive to handle other than as a solution or dilute slurry in excess solvent, and then only on 1 g scale.
See other BIS(ARENEDIAZO) SULFIDES

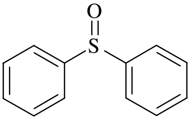
3486. Diphenyl ether
[101-84-8] **$C_{12}H_{10}O$**



HCS 1980, 731

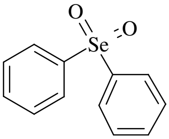
Chlorosulfuric acid
See Chlorosulfuric acid: Diphenyl ether

3487. Diphenyl sulfoxide
[945-51-7] **$C_{12}H_{10}OS$**



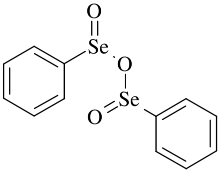
Acetonitrile, Trichlorosilane
See Trichlorosilane: Acetonitrile, etc.

3488. Diphenylselenone
[10504-99-1] **$C_{12}H_{10}O_2Se$**



Krafft, F. *et al., Ber.*, 1896, **29**, 424
It explodes feebly on heating in a test tube.
See related NON-METAL OXIDES

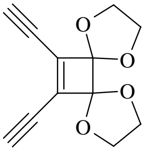
3489. Benzeneseleninic anhydride
[17697-12-0] **$C_{12}H_{10}O_3Se_2$**



Benzhydrazide
See Benzeneseleninic acid: Hydrazine derivatives
See other ACID ANHYDRIDES

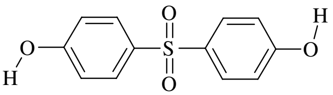
Preparative hazard
See Hydrogen peroxide: Diphenyl diselenide

3490. 11,12-Diethynyl-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene
[123002-93-7] **$C_{12}H_{10}O_4$**



See cis-3,4-Diethynylcyclobut-3-ene-1,2-diol
See Oligo(octacarbondioxide)
See other ACETYLENIC COMPOUNDS

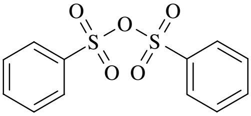
3491. Bis(4-hydroxyphenyl) sulfone
[80-09-1] **$C_{12}H_{10}O_4S$**



When prepared by thermal dehydration of 4-hydroxybenzenesulfonic acid, the reaction mixture begins to decompose exothermally around 240°C. Decomposition is delayed but still occurs at lower temperatures (160°C), and the presence of iron reduces the time to maximum rate of decomposition. Above 800 ppm of iron, the time to maximum rate is less than the dehydration reaction time, leading to severe control problems. Improved processing conditions were developed.
See entry SELF-ACCELERATING REACTIONS
See other INDUCTION PERIOD INCIDENTS

3492. Benzenesulfonic anhydride

[512-35-6] **$C_{12}H_{10}O_5S_2$**



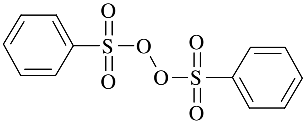
Hydrogen peroxide

See Hydrogen peroxide: Benzenesulfonic anhydride

See other ACID ANHYDRIDES

3493. Dibenzenesufonyl peroxide

[29342-61-8] **$C_{12}H_{10}O_6S_2$**



Alone, or Nitric acid, or Water

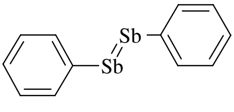
1. Davies, 1961, 65
2. Crovatt, L. W. *et al., J. Org. Chem.*, 1959, **24**, 2032
3. Weinland, R. F. *et al., Ber.*, 1903, **36**, 2702

It explodes at 53—54°C [1], and decomposes somewhat violently after storage overnight at ambient temperature, but may be stored unchanged for several weeks at —20°C [2]. It is also shock-sensitive, and explodes with fuming nitric acid, or addition to boiling water [3].

See other DIACYL PEROXIDES

3494. Diphenyldistibene (Stibobenzene)

[5702-61-4] **$C_{12}H_{10}Sb_2$**



Air, or Nitric acid

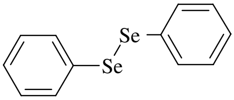
Schmidt, H., *Ann.*, 1920, **421**, 235

This antimony analogue of azobenzene ignites in air, and is oxidised explosively by nitric acid.

See related ARYLMETALS, AZO COMPOUNDS

3495. Diphenyl diselenide

[1666-13-3] **$C_{12}H_{10}Se_2$**

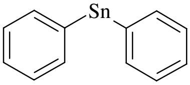


Hydrogen peroxide

See Hydrogen peroxide: Diphenyl diselenide

3496. Diphenyltin

[6381-06-2] **$C_{12}H_{10}Sn$**



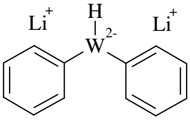
Nitric acid

See Nitric acid: Diphenyltin

See other ARYLMETALS

3497. Lithium diphenylhydridotungstate(2—)

[ ] **$C_{12}H_{11}Li_2W$**



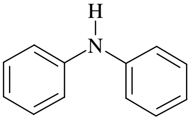
Sanny, B., *Z. Anorg. Chem.*, 1964, **329**, 221

It is pyrophoric in air.

See related ARYLMETALS, METAL HYDRIDES

3498. Diphenylamine

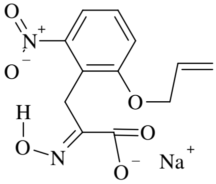
[122-39-4] **$C_{12}H_{11}N$**



Preparative hazard

See Aniline: Anilinium chloride

3499. Sodium 2-allyloxy-6-nitrophenylpyruvate oxime
[80841-08-3] **$C_{12}H_{11}N_2NaO_6$**



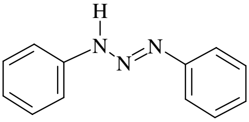
Hydrochloric acid

Lading, P. *et al., Dan. Kemi*, 1981, **62**, 242—244

Conversion of the sodium salt to the free acid by hydrochloric acid treatment led to an explosion. This was attributed to the thermal instability of the acid, and its Claisen rearrangement to 3-allyl-2-hydroxynitrotoluene, identified in the residue.

See other ALLYL COMPOUNDS, NITROARYL COMPOUNDS, OXIMES

3500. 1,3-Diphenyltriazene
[136-35-6] **$C_{12}H_{11}N_3$**



1. Müller, E. *et al., Chem. Ber.*, 1962, **95**, 1257
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
3. Grewer, T. *et al., Proc. 4th Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, A1—A11, Rugby, IChE, 1983
4. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
5. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987

It decomposes explosively at the m.p., 98°C [1], and shows a high rate of pressure increase on exothermic decomposition [2]. The heat of decomposition was determined as 1.34 kJ/g by DSC, and T_{ait24} was determined as 88°C by adiabatic Dewar tests, with an apparent energy of activation of 223 kJ/mol [3]. When finely divided, it also shows significant dust explosion hazards, with a maximum explosion pressure of 7.75 bar, and a maximum rate of pressure rise above 680 bar/s [4]. Further work on homogeneous decomposition under confinement has been reported [5].

Acetic anhydride

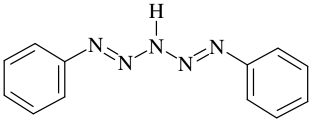
Heusler, F., *Ber.*, 1891, **24**, 4160

A mixture exploded with extraordinary violence on warming.

See other TRIAZENES

3501. 1,5-Diphenylpentaazadiene

[ ] $C_{12}H_{11}N_5$



Griess, P., *Ann.*, 1866, **137**, 81

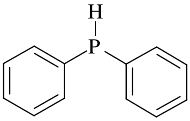
The dry solid explodes violently on warming, impact or friction, and *C*-homologues behave similarly.

See other HIGH-NITROGEN COMPOUNDS

See related TRIAZENES

3502. Diphenylphosphine

[829-85-6] $C_{12}H_{11}P$



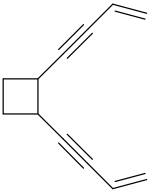
Ireland, R. F. *et al., Org. Synth.*, 1977, **56**, 47

If the phosphine is spilled onto a paper towel (or other extended surface), it may ignite in air.

See related ALKYLPHOSPHINES

3503. 1,2-Di(3-buten-1-ynyl)cyclobutane

cis [80605-27-2], trans [80605-36-3] $C_{12}H_{12}$



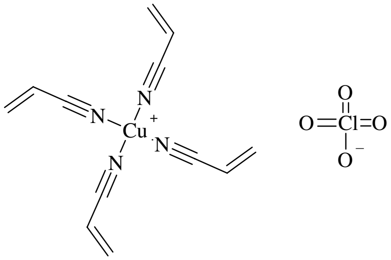
Cupery, M. E. *et al., J. Amer. Chem. Soc.*, 1934, **56**, 1167

During isolation of the title product from polymerised 1,5-hexadiene-3-yne, high vacuum distillation must be carried only to a limited extent to prevent sudden explosive decomposition of the more highly polymerised residue.

See other ACETYLENIC COMPOUNDS, POLYMERISATION INCIDENTS

3504. Tetraacrylonitrilecopper(I) perchlorate

[ ] **$C_{12}H_{12}ClCuN_4O_4$**



Ondrejovic, G., *Chem. Zvesti*, 1964, **18**, 281

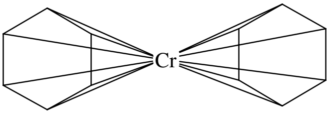
Like the copper(II) analogue, it decomposes explosively on heating

See other CYANO COMPOUNDS

See related AMMINEMETAL OXOSALTS

3505. Bis(η-benzene)chromium(0)

[1271-54-1] **$C_{12}H_{12}Cr$**



Oxygen

Anon., *Chem. Eng. News*, 1964, **42**(38), 55

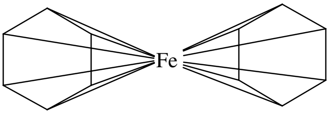
The orange-red complex formed with oxygen in benzene decomposes vigorously on friction or heating in air.

See other ORGANOMETALLICS

See related ARYLMETALS

3506. Bis(η-benzene)iron(0)

[68868-87-1] **$C_{12}H_{12}Fe$**



Timms, P. L., *Chem. Eng. News*, 1969, **47**(18), 43

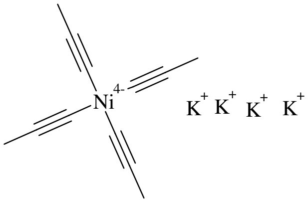
Prepared in the vapour phase at low temperature, the solid explodes at —40°C.

See other ORGANOMETALLICS

See related ARYLMETALS

3507. Potassium tetrakis(propynyl)nickelate(4—)

[ ] **$C_{12}H_{12}K_4Ni$**



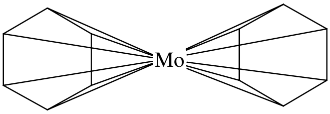
Ammonia

The diammoniate ignites on friction, impact or flame contact.

See entry COMPLEX ACETYLIDES

3508. Bis(η-benzene)molybdenum(0)

[12129-68-9] **$C_{12}H_{12}Mo$**



Silverthorn, W. E., *Inorg. Synth.*, 1977, **17**, 56

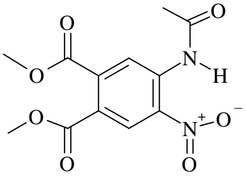
The dry crude material is highly pyrophoric in air.

See other ORGANOMETALLICS

See related ARYLMETALS

3509. Dimethyl 4-acetamino-5-nitrophthalate

[52412-56-3] **$C_{12}H_{12}N_2O_7$**



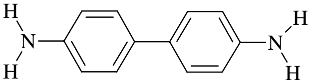
Preparative Hazard

See Nitric acid: Dimethyl 4-acetamidophthalate

See other NITROARYL COMPOUNDS

3510. Benzidine (4,4′-Diaminobiphenyl)

[92-87-5] **$C_{12}H_{12}N_2$**

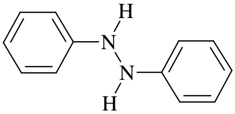


Nitric acid

See Nitric acid: Benzidine

3511. 1,2-Diphenylhydrazine

[530-50-7] **$C_{12}H_{12}N_2$**



Energy of decomposition (in range 135—405°C) measured as 0.442 kJ/g by DSC, and T_{ait24} was determined as 131°C by adiabatic Dewar tests, with an apparent energy of activation of 139 kJ/mol.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

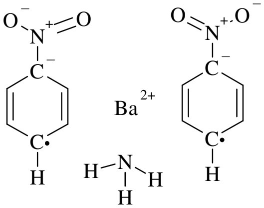
Perchloryl fluoride

See Perchloryl fluoride: Nitrogenous bases

See other REDUCANTS

3512. Amminebarium bis(nitrophenylide)

[91410-67-2] **$C_{12}H_{13}BaN_3O_4$**



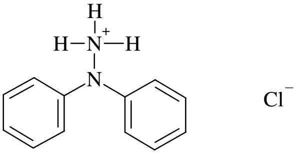
Stevenson, G. R. *et al., J. Org. Chem.*, 1984, **49**, 3444

A 5 day old sample of the crystalline radical complex exploded violently on agitation.

See related N-METAL DERIVATIVES, NITROARYL COMPOUNDS

3513. 1,1-Diphenylhydrazinium chloride

[530-47-2] **$C_{12}H_{13}ClN_2$**

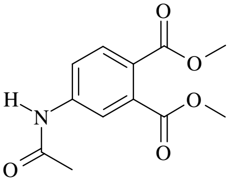


Energy of decomposition (in range 140—200°C) measured as 0.59 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

3514. Dimethyl 4-acetamidophthalate

[51832-56-5] **$C_{12}H_{13}NO_5$**



Nitric acid

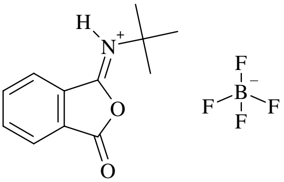
Anon., *Jahresber.*, 1987, 64

Nitration of the ester with 90% nitric acid was effected according to a literature method. Examination of the reaction mixture by TLC showed that both expected mononitro derivatives had been formed, and it was allowed to stand at ambient temperature overnight. Ice and dichloromethane were then added, and the separated solvent layer was washed with aqueous sodium hydrogen carbonate, dried, and then freed of solvent by evaporation. The viscous oily residue decomposed and ignited in the flask. The preparation was repeated, but worked up immediately and under nitrogen while still cold, and furnished samples of both of the pure isomeric nitro derivatives. Thermal analysis of these showed both to be thermally stable. It was concluded that the decomposition was due to an impurity formed during the 16 h interval between nitration and work-up.

See other NITRATION INCIDENTS

3515. *N-tert*-Butylphthalisoimidium tetrafluoroborate (3-*N-tert*-Butyliminioisobenzofuranone tetrafluoroborate)

[69338-55-2] **$C_{12}H_{14}BF_4NO_2$**

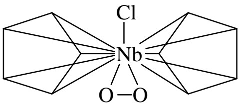


Preparative hazard

See Acetic anhydride: *N-tert*-Butylphthalamic acid, etc.

3516. Bis(methylcyclopentadienyl)peroxoniobium chloride

[77625-37-7] **$C_{12}H_{14}ClNbO_2$**



Sala-Pala, J. *et al., J. Mol. Catal.*, 1980, **7**, 142

Occasionally the dry product exploded violently when scraped off the glass container. It invariably exploded when irradiated with a Raman laser beam, even at —80°C.
See other IRRADIATION DECOMPOSITION INCIDENTS
See related ORGANOMETALLIC PEROXIDES

3517. Dianilineoxodiperoxochromium(VI)

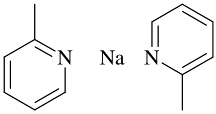
[ ] **$C_{12}H_{14}CrN_2O_5$**

$[(PhNH_2)_2CrO(O_2)_2]$

See Oxodiperoxodipyridinechromium(VI)
See other AMMINECHROMIUM PEROXOCOMPLEXES

3518. Bis(2-methylpyridine)sodium

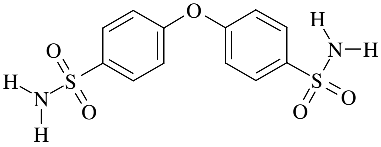
[ ] **$C_{12}H_{14}N_2Na$**



Sidgwick, 1950, 89
The addition product of sodium and 2-methylpyridine (or pyridine) ignites in air.

3519. 4,4′-Oxybis(benzenesulfonylhydrazide)

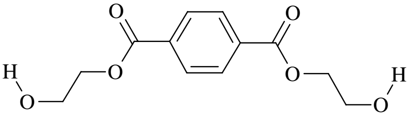
[80-51-3] **$C_{12}H_{14}N_4O_5S_2$**



The more recently calculated value of 78°C for critical ignition temperature is appreciably lower than the previous value of 90°C.
See entry BLOWING AGENTS, CRITICAL IGNITION TEMPERATURE (reference 2)
See other N—S COMPOUNDS

3520. Bis(2-hydroxyethyl) terephthalate

[959-26-2] **$C_{12}H_{14}O_6$**

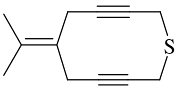


Ethanol, Perchloric acid

See Perchloric acid: Bis(2-hydroxyethyl) terephthalate, etc.

3521. 6-Isopropylidenethiacyclodeca-3,8-diyne

[ ] **$C_{12}H_{14}S$**



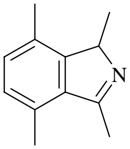
Gleiter, R. *et al., Synthesis*, 1993, (6), 558

The compound exploded during Kugelrohr distillation at about 1 millibar, temperature not stated but probably about 100°C.

See other ACETYLENIC COMPOUNDS

3522. 1,3,4,7-Tetramethylisoindole

[20944-65-4] **$C_{12}H_{15}N$**



Cobalt

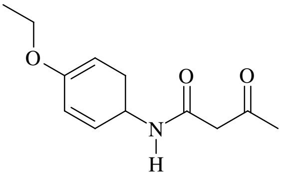
Dolphin, D. *et al., Inorg. Synth.*, 1980, **20**, 157

The scale of the procedure described for preparing [octamethyltetrabenzoporphinato(2—)]cobalt(II) by heating the reagents in an evacuated Carius tube at 390°C must not be increased or the tube will explode. Personal protection is also necessary when opening the sealed tube.

See other ORGANIC BASES

3523. Acetoacet-4-phenetidide

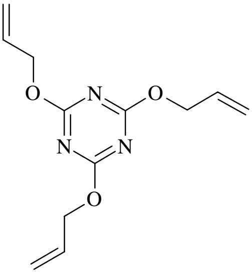
[122-82-7] **$C_{12}H_{15}NO_3$**



The fine powder is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

3524. 2,4,6-Triallyloxy-1,3,5-triazine ('Triallyl cyanurate')
[1025-15-6] **$C_{12}H_{15}N_3O_3$**

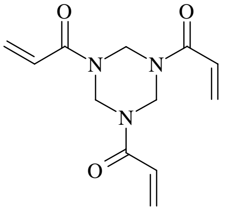


Preparative hazard

See 2,4,6-Trichloro-1,3,5-triazine: Allyl alcohol

See other ALLYL COMPOUNDS

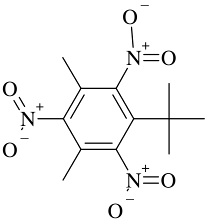
3525. 1,3,5-Tris(1-oxoprop-2-enyl)-hexahydro-1,3,5-triazine (1,3,5-Triacrylylhexahydro-*sym*-triazine)
[959-52-4] **$C_{12}H_{15}N_3O_3$**



Preparative Hazard

See Acrylonitrile: Formaldehyde

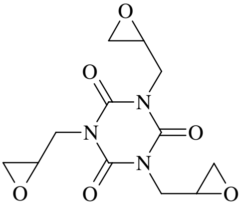
5326. 5-*tert*-Butyl-2,4,6-trinitro-1,3-xylene
[81-15-2] **$C_{12}H_{15}N_3O_6$**



See Nitric acid: *tert*-Butyl-*m*-xylene, Sulfuric acid

See other POLYNITROARYL COMPOUNDS

3527. 1,3,5-Tris(2,3-epoxypropyl)triazine-2,4,6-trione ('Triglycidyl isocyanurate') [2589-01-7] $C_{12}H_{15}N_3O_6$

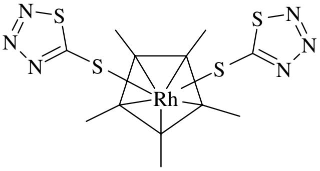


Anon., *Loss Prev. Bull.*, 1977, (013), 3

The epoxy resin component is made by a 2-stage process involving reaction of 1-chloro-2,3-epoxypropane (epichlorhydrin) with isocyanuric acid to give the 1,3,5-tris(2-hydroxy-3-chloropropyl) derivative, which is then treated with sodium hydroxide to eliminate hydrogen chloride to form the title compound. One batch contained more than the normal amount of hydrolysable chlorine, and when excess epichlorhydrin was distilled off, the residual material decomposed with explosive violence. It was later established that the abnormal chlorine content was associated with reduced thermal stability, and criteria for hydrolysable chlorine, epoxy content and pH have been set to prevent distillation of off-spec. material.

See other 1,2-EPOXIDES

3528. Pentamethylcyclopentadienyl-bis(thiolatothiatriazyl)rhodium [71178-86-4] $C_{12}H_{15}N_6RhS_4$

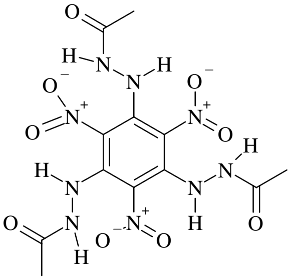


Rigby, W. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 378

The material, which is probably polymeric, may detonate.

See other ORGANOMETALLICS, N—S COMPOUNDS

3529. 2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene [78925-61-8] $C_{12}H_{15}N_9O_9$



Hydrochloric acid

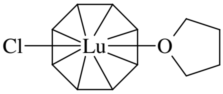
Lawrence, G. W. *et al., Tetrahedron Lett.*, 1980, **21**, 1618

Hydrolysis of the acetylhydrazide by 12M hydrochloric acid at ambient temperature gave a solid product which was surprisingly sensitive to a mild hammer-blow. Formation of a diazo structure was suspected.

See other DIAZONIUM SALTS, POLYNITROARYL COMPOUNDS

3530. Chloro(η^8 1,3,5,7-cyclooctatetraene)(tetrahydrofuran)lutetium

[96504-50-6] **$C_{12}H_{16}ClLuO$**

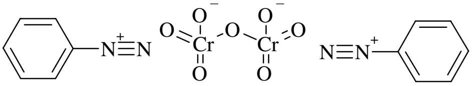


1. Wayda, A. L., *Inorg. Synth.*, 1990, **27**, 150
2. The dry powder may ignite spontaneously in air, partially oxidised samples can explode.

See other ORGANOMETALLICS

3531. Dianilinium dichromate

[101672-09-7] **$C_{12}H_{16}Cr_2N_2O_7$**



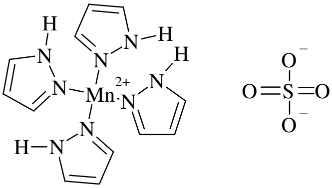
Gibson, G. M., *Chem. & Ind.*, 1966, 553

It is unstable on storage.

See other DICHROMATE SALTS OF NITROGENOUS BASES

3532. Tetrakis(pyrazole)manganese(II) sulfate

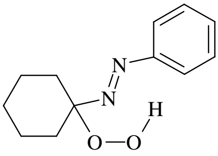
[ ] **$C_{12}H_{16}MnN_8O_4S$**



See entry AMMINEMETAL OXOSALTS (reference 9)

3533. 1-Phenylazocyclohexyl hydroperoxide

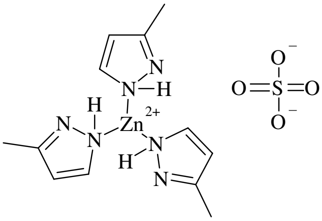
[950-32-3] **$C_{12}H_{16}N_2O_2$**



See entry α-PHENYLAZO HYDROPEROXIDES (reference 4)

3534. Tris(3-methylpyrazole)zinc sulfate

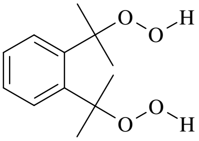
[55060-80-5] **$C_{12}H_{18}N_6O_4SZn$**



See entry AMMINEMETAL OXOSALTS (reference 9)

3535. 1,2-Bis(2-hydroperoxy-2-propyl)benzene

[29014-32-2] **$C_{12}H_{18}O_4$**



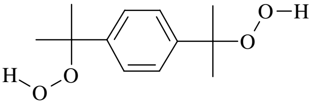
Velenskii, M. S. *et al., Chem. Abs.*, 1974, **81**, 108066

These difunctional analogues of cumyl hydroperoxide appear to be no more hazardous that the latter. Though impact-sensitive, the decomposition was mild and incomplete.

See other ALKYL HYDROPEROXIDES

3536. 1,4-Bis(2-hydroperoxy-2-propyl)benzene

[3159-98-6] **$C_{12}H_{18}O_4$**

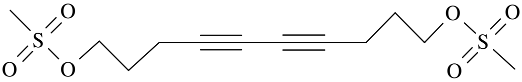


Velenskii, M. S. *et al., Chem. Abs.*, 1974, **81**, 108066

These difunctional analogues of cumyl hydroperoxide appear to be no more hazardous that the latter. Though impact-sensitive, the decomposition was mild and incomplete.
See other ALKYL HYDROPEROXIDES

3537. 1,10-Di(methanesulfonyloxy)deca-4,6-diyne

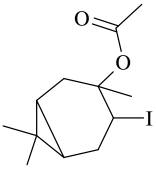
[42404-59-1] **$C_{12}H_{18}O_6S_2$**



CHETAH, 1990, 189
Shock sensitive. The parent diol is not but shows thermal risks on calorimetry.
See other ACETYLENIC COMPOUNDS, SULFUR ESTERS

3538. 3-Acetoxy-4-iodo-3,7,7-trimethylbicyclo[4.1.0]heptane

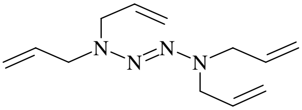
[ ] **$C_{12}H_{19}IO_2$**



See vic-IODO-ALKOXY COMPOUNDS
See other IODINE COMPOUNDS

3539. Tetraallyl-2-tetrazene (Tetra-2-propenyl-2-tetrazene)

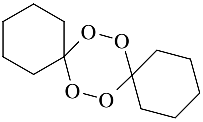
[52999-19-6] **$C_{12}H_{20}N_4$**



Houben-Weyl, 1967, Vol. 10.2, 831
It explodes with great violence when heated above its b.p., 113°C/1 bar.
See other ALLYL COMPOUNDS, TETRAZENES

3540. 3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane (7,8,15,16-Tetraoxadispiro[5.2.5.2]hexadecane)

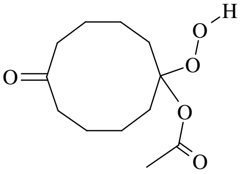
[183-84-6] **$C_{12}H_{20}O_4$**



Dilthey, W. *et al., J. Prakt. Chem.*, 1940, **154**, 219
This dimeric cyclohexanone peroxide explodes on impact.
See other CYCLIC PEROXIDES

3541. 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide

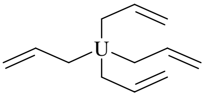
[ ] **$C_{12}H_{20}O_5$**



Criegee, R. *et al., Ann.*, 1949, **564**, 15
The crystalline compound prepared at —70°C explodes mildly after a few minutes at ambient temperature.
See related ALKYL HYDROPEROXIDES, 1-OXYPEROXY COMPOUNDS

3542. Tetraallyluranium

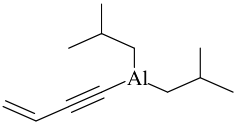
[28711-64-0] **$C_{12}H_{20}U$**



Bailar, 1973, Vol. 5, 405
Only stable below —20°C, it ignites in air.
See other ALLYL COMPOUNDS
See related ALKYLMETALS

3543. 3-Buten-1-ynyldiisobutylaluminium

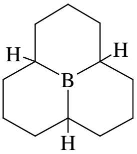
[18864-05-6] **$C_{12}H_{21}Al$**



Petrov, A. A. *et al., Zh. Obsch. Khim.*, 1962, **32**, 1349
It ignites in air.
See other METAL ACETYLIDES, TRIALKYLALUMINIUMS

3544. Perhydro-9*b*-boraphenalene

[16664-33-8] **$C_{12}H_{21}B$**



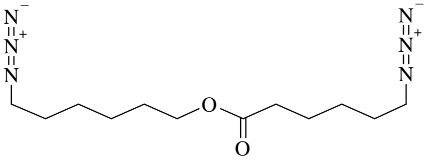
Negishi, E.-I. *et al., Org. Synth.*, 1983, **61**, 103—111

The title product and several precursors are highly pyrophoric, and all leaks must be eliminated from vacuum handling equipment.

See related ALKYLBORANES

3545. 6-Azidohexyl 6-azidohexanoate

[84487-84-3] **$C_{12}H_{22}N_6O_2$**

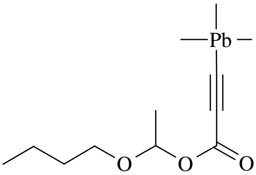


See entry ENERGETIC COMPOUNDS

See other ORGANIC AZIDES

3546. 1-Butoxyethyl 3-trimethylplumbylpropiolate

[21981-95-3] **$C_{12}H_{22}O_3Pb$**



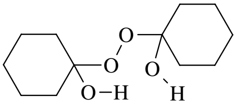
Houben-Weyl, 1975, Vol. 13.3, 80

It is explosive.

See related ALKYLMETALS, METAL ACETYLIDES

3547. Bis(1-hydroxycyclohexyl) peroxide (1,1′-Dioxybiscyclohexanol)

[2407-94-5] **$C_{12}H_{22}O_4$**



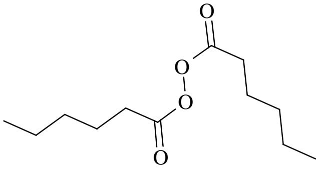
1. Stoll, M. *et al., Helv. Chim. Acta*, 1930, **13**, 142
2. *CHETAH*, 1990, 183

Normally stable, it explodes on attempted vacuum distillation [1] and is shock sensitive [2].

See other 1-OXYPEROXY COMPOUNDS

3548. Dihexanoyl peroxide

[2400-59-1] **$C_{12}H_{22}O_4$**



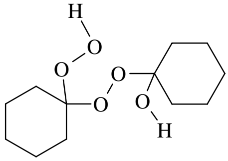
Castrantas, 1965, 17

It explodes at 85°C.

See other DIACYL PEROXIDES

3549. 1-Hydroperoxy-1′-hydroxydicyclohexyl peroxide (1-[(1-Hydroperoxycyclohexyl)dioxy]cyclohexanol)

[78-18-2] **$C_{12}H_{22}O_5$**



1. Davies, 1961, 74
2. Cardinale, G. *et al., Tetrahedron*, 1985, **45**, 2901

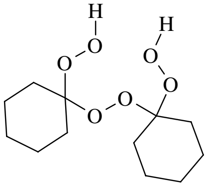
This appears to be a main constituent of commercial ‘cyclohexanone peroxide’ together with the bis(hydroperoxy) peroxide (below), and is also known to be hazardous [1]. Prepared from cyclohexanone and 30% hydrogen peroxide in presence of hydrochloric acid catalyst, it must be kept moist after isolation as it may explode on drying out [2].

See entry COMMERCIAL ORGANIC PEROXIDES

See other 1-OXYPEROXY COMPOUNDS

3550. Bis(1-hydroperoxycyclohexyl) peroxide
(Dioxydicyclohexylidenebishydro-peroxide)

[2699-12-9] **$C_{12}H_{22}O_6$**



Criegee, R. *et al., Ann.*, 1949, **565**, 17—18

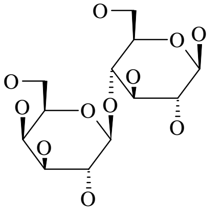
One of the components in 'cyclohexanone peroxide', it explodes violently at elevated temperatures (during vacuum distillation or on exposure to flame).

See entry COMMERCIAL ORGANIC PEROXIDES

See other 1-OXYPEROXY COMPOUNDS

3551. Lactose

[63-42-3] **$C_{12}H_{22}O_{11}$**



Alkalis

See SUGARS

Oxidants

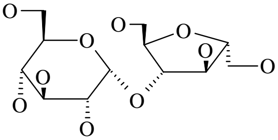
Treumann, H., *Chem. Abs.*, 1981, **94**, 177551

Explosion hazards of mixtures of lactose monohydrate with potassium chlorate, potassium nitrate or potassium perchlorate are assessed.

See Potassium chlorate: Sugars

3552. Sucrose

[57-50-1] **$C_{12}H_{22}O_{11}$**



1. Geysen, W. J. *et al., ASTM Spec. Tech. Publ. 958*, 234-242, Philadelphia, ASTM, 1987
2. Beck, H., *Gefahrstoffe-Reinhalt. Luft*, 1996, **56**(10), 369

3. Markowski, A., *Chem. Abs.*, 2000, **132**, 349186d
4. Rearick D. E. *et al., Chem. Abs.*, 1999, **131**, 355274b

The investigation of a sugar dust explosion in a Belgian factory is discussed and preventive and protective measures are described in detail [1]. Sugar dust explosions and safety measures against them are reviewed [2]. It is calculated that there is a significant risk of explosion from a runaway Maillard reaction (condensation of sugars with aminoacids or proteins) during sugar manufacture [3]. A factory explosion attributed to simple decomposition of sugar has been reported [4].

Energy of decomposition (in range 280—350°C) measured as 0.48 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See other DUST EXPLOSION INCIDENTS

Nitric acid

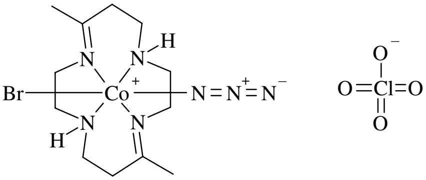
See Nitric acid: Sucrose

Sulfuric acid

See Sulfuric acid: Sucrose

3553. *trans*-Bromoazido(meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) perchlorate

[74190-87-7] **$C_{12}H_{24}BrClN_7O_4$**



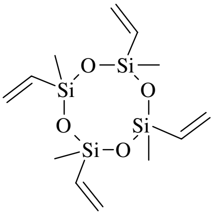
Lawrence, G. A. *et al., Aust. J. Chem.*, 1980, **33**, 274

Perchlorate salts of the azide complexes, and also of the dichloro analogue, may present an explosion hazard.

See related [14] DIENE-N_4COMPLEXES

3554. 2,4,6,8-Tetraethenyl-2,4,6,8-tetramethylcyclotetrasiloxane.

[2554-06-5] **$C_{12}H_{24}O_4Si_4$**



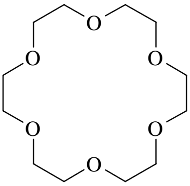
Rubinsztajn, S. *et al., Chem. Eng. News.*, 1994, **72**(17), 4

Hydrosilylation with 2,4,6,8-tetramethylcyclotetrasiloxane has sometimes given uncontrollable exotherms or explosions in the laboratory. Use of safety screens and the lowest possible (< 20 ppm) level of platinum catalyst are recommended.

See VINYLSILOXANES

3555. 1,4,7,10,13,16-Hexaoxacyclooctadecane ('18-Crown-6')

[17455-13-9] **$C_{12}H_{24}O_6$**



Preparative hazard

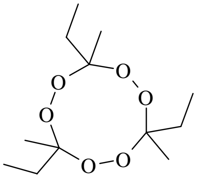
1. Cram, D. J. *et al., J. Org. Chem.*, 1974, **39**, 2445
2. Stott, P. E., *Chem. Eng. News*, 1976, **54**(37), 5
3. Gouw, T. H., *Chem. Eng. News*, 1976, **54**(44), 5
4. Stott, P. E., *Chem. Eng. News*, 1976, **54**(51), 5
5. de Jong, F. *et al., J. R. Neth. Chem. Soc.*, 1981, **100**, 449—452

There is a potential explosion hazard during larger scale operation of the published (small-batch) procedure [1]. This arose during thermal decomposition of the crown ether—potassium chloride complex under reduced pressure, when the crude ether distilled out. The larger batch size involved more extensive heating to complete the decomposition of the complex, and a considerable amount of 1,4-dioxane was produced by cracking and blocked the vacuum pump trap. Admission of air to the overheated residue led to a violent explosion, attributed to autoignition of the dioxane—air mixture. Dioxane has a relatively low AIT (180°C) and rather wide explosive limits. Practical precautions are detailed [2]. Subsequently the observed hazards were attributed to poor distillation procedures [3], but further more detailed information on the experimental procedure was published to refute this view [4]. A safe method of purifying the product without distillation involves formation of complexes with alkaline earth metal alkanedisulfonates [5].

See other APROTIC SOLVENTS

3556. 3,6,9-Triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexoxonane

[24748-23-0] **$C_{12}H_{24}O_6$**

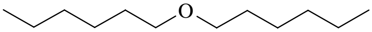


See 3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane

See other CYCLIC PEROXIDES

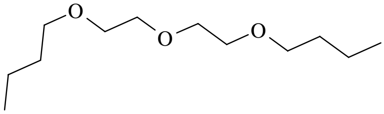
†3557. Dihexyl ether

[112-58-3] **$C_{12}H_{26}O$**



3558. Di-2-butoxyethyl ether

[112-73-2] **$C_{12}H_{26}O_3$**

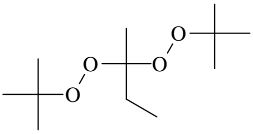


Nitric acid

See Nitric acid: Di-2-butoxyethyl ether

3559. 2,2-Di(*tert*-butylperoxy)butane

[2167-23-9] **$C_{12}H_{26}O_4$**



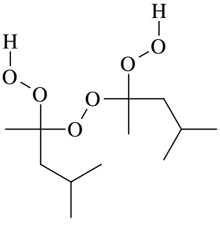
Dickey, F. H. *et al., Ind. Eng. Chem.*, 1949, **41**, 1673

The pure material explodes on heating to about 130°C, on sparking or on impact.

See related DIALKYL PEROXIDES

3560. Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide

[53151-88-5] **$C_{12}H_{26}O_6$**



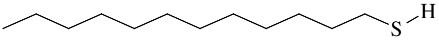
Leleu, *Cahiers*, 1973, (71), 238

The triperoxide, main component in 'MIBK peroxide', is explosive in the pure state, but insensitive to shock as the commercial 60% solution in dimethyl phthalate. The solution will explode at about 75°C, and slowly liberates oxygen at ambient temperatures.

See KETONE PEROXIDES

See related ALKYL HYDROPEROXIDES, DIALKYL PEROXIDES

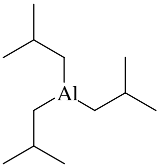
3561. Dodecanethiol
[1322-36-7] **$C_{12}H_{26}S$**



HCS 1980, 449

Nitric acid
See Nitric acid: Alkanethiols
See other ALKANETHIOLS

†3562. Triisobutylaluminium
[100-99-2] **$C_{12}H_{27}Al$**

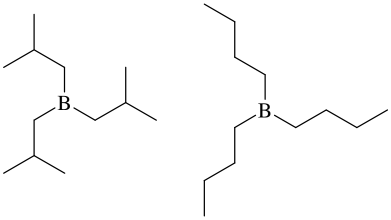


HCS 1980, 937

1. ‘Specialty Reducing Agents’, Brochure TA-2002/1, New York, Texas Alkyls, 1971
2. Fischer, T. S. *et al.*, *Int. Annu. Conf. ICT*, 1996, **27th**(Energetic Materials), 107

Used industrially as a powerful reducant, it is supplied as a solution in hydrocarbon solvents. The undiluted material is of relatively low thermal stability (decomposing above 50°C) and ignites in air unless diluted to below 25% concentration [1]. A thermal explosion of the compound has been studied from a theoretical standpoint [2].
See other TRIALKYLALUMINIUMS

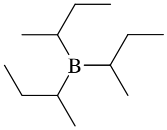
3563. *mixo*-Tributylborane
[122-56-5, 1116-39-8] (n-, iso- resp.) **$C_{12}H_{27}B$**



1. Hurd, D. T., *J. Amer. Chem. Soc.*, 1948, **70**, 2053
2. Brown, C. A., *Inorg. Synth.*, 1977, **17**, 27

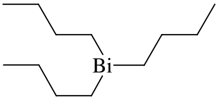
A mixture of the n- and iso- compounds ignited on exposure to air [1]. In bulk, the liquid does not ignite in air, but may do so when absorbed onto a porous surface like paper, or if spread as a thin film [2].
See other ALKYLBORANES

3564. Tri-2-butylborane
[1113-78-6] **$C_{12}H_{27}B$**



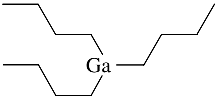
Brown, C. A., *Inorg. Synth.*, 1977, **17**, 27
It ignites in air.
See other ALKYLBORANES

3565. Tributylbismuth
[3692-81-7] **$C_{12}H_{27}Bi$**



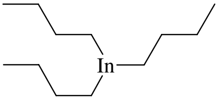
Air, or Oxygen
Gilman, H. *et al., J. Amer. Chem. Soc.*, 1939, **61**, 1170
It ignites in air and explodes violently in oxygen.
See other TRIALKYLBISMUTHS

3566. Tributylgallium
[15677-44-8] **$C_{12}H_{27}Ga$**



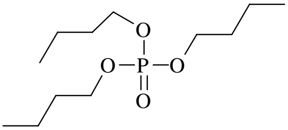
Kovar, R. A. *et al., Inorg. Chem.*, 1980, **19**, 3265
Tributylgallium and dibutylgallium chloride are probably pyrophoric in air.
See other ALKYLMETALS

3567. Tributylindium
[15676-66-1] **$C_{12}H_{27}In$**



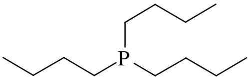
Houben-Weyl, 1970, Vol. 13.4, 347
It ignites in air.
See other ALKYLMETALS

3568. Tributyl phosphate
[126-73-8] **$C_{12}H_{27}O_4P$**



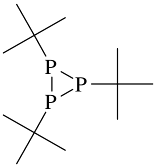
Nitric acid, Nitrates
See NUCLEAR WASTES

†3569. Tributylphosphine
[998-40-3] **$C_{12}H_{27}P$**



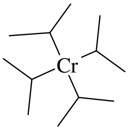
Steele, A. B. *et al., Chem. Engrg.*, 1969, **66**(4), 160
It ignites in air.
See other ALKYLPHOSPHINES

3570. Tris(2,2-dimethylethyl)triphosphirane
[61695-12-3] **$C_{12}H_{27}P_3$**



Baudler, M. *et al., Inorg. Synth.*, 1989, **25**, 1
The compound is reported as pyrophoric when finely divided.
See related ALKYLPHOSPHINES

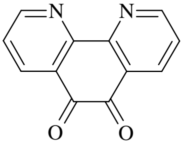
3571. Tetraisopropylchromium
[38711-69-2] **$C_{12}H_{28}Cr$**



Müller, J. *et al., Angew. Chem. (Intern. Ed.)*, 1975, **14**, 761
The finely crystalline form is pyrophoric.
See other ALKYLMETALS

3572. 1,10-Phenanthroline-5,6-dione

[27318-90-7] **$C_{12}H_8N_2O_2$**



Preparative hazard

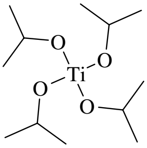
Black, K. J. *et al., Inorg. Chem.*, 1993, **32**(24), 5591-6

Preparation by oxidising tris(phenanthroline)cobalt(III) tetrafluoroborate with nitric acid in sulfuric acid with potassium bromide catalysis is potentially explosive.

See Nitric acid

3573. Titanium tetraisopropoxide

[546-68-9] **$C_{12}H_{28}O_4Ti$**



HCS 1980, 894

Hydrazine

See Hydrazine: Titanium compounds

See other METAL ALKOXIDES

3574. 'Tetrapropyldiborane'

[22784-01-6] **$C_{12}H_{30}B_2$**

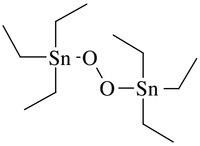
Complex Structure

See 'TETRAETHYLDIBORANE'

See other ALKYLBORANES

3575a. Bis(triethyltin) peroxide

[4403-63-8] **$C_{12}H_{30}O_2Sn_2$**



Sorbe, 1968, 160

Readily decomposed, it explodes at 50°C.

See other ORGANOMETALLIC PEROXIDES

3575b. 2,3,4,5,6,7,8,9,10,11-Decamethyl-1,12-dicarbadodecaborane

[168098-42-8] **$C_{12}H_{32}B_{10}$**

Complex Structure

See other BORANES

Fluorine

Axel, K. *et al., Angew. Chem. (Int.)*, 2001, **40**(11), 2121

Fairly complete fluorination gave a mixture of the fully fluorinated, the deca(trifluoromethyl) and the deca(trifluoromethyl)monofluoro compounds. This product exploded when scraped with a spatula. It subsequently proved possible to isolate the deca(trifluoromethyl) component. This too exploded on scraping, but not from percussion.

3576. Tetra(3-aminopropanethiolato)trimercury perchlorate

[95247-08-8] **$C_{12}H_{32}Cl_2Hg_3O_8S_4$**

$[(H_2NC_3H_6S)_4Hg_3]\ [ClO_4]_2$

Barrera, H. *et al., Chem. Abs.*, 1985, **102**, 159407

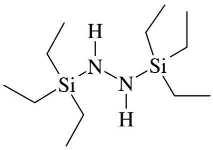
It decomposed violently but non-explosively.

See other MERCURY COMPOUNDS

See related AMMINEMETAL OXOSALTS

3577. 1,2-Bis(triethylsilyl)hydrazine

[13271-97-1] **$C_{12}H_{32}N_2Si_2$**

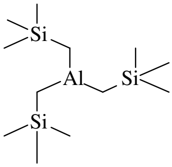


See entry SILYLHYDRAZINES

See related ALKYLSILANES

3578a. Tris(trimethylsilylmethyl)aluminium

[41924-27-0] **$C_{12}H_{33}AlSi_3$**



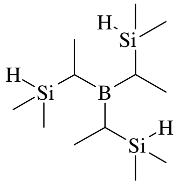
Tessier-Youngs, C. *et al., Inorg. Synth.*, 1986, **24**, 92, 94

It burns spontaneously in air and reacts violently with water, as does the congener, bis(trimethylsilylmethyl)aluminium bromide.

See related ALKYLMETALS, ALKYLSILANES, TRIALKYLALUMINIUMS

3578b. Tris[1-(dimethylsilyl)ethyl]borane

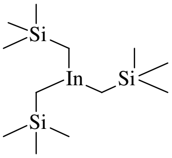
[256453-51-7] **$C_{12}H_{33}BSi_3$**



See Tris(1-silylethyl)borane

3579. Tris(trimethylsilylmethyl)indium

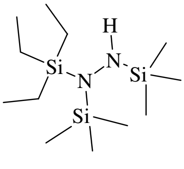
[69833-15-4] **$C_{12}H_{33}InSi_3$**



Kopasz, J. P *et al., Inorg. Synth.*, 1986, **24**, 89
It burns spontaneously in air.
See related ALKYLMETALS, ALKYLSILANES, TRIALKYLALUMINIUMS

3580. Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine

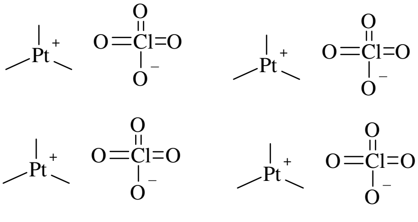
[13272-03-2] **$C_{12}H_{34}N_2Si_3$**



See entry SILYLHYDRAZINES
See related ALKYLSILANES

3581. Dodecamethyltetraplatinum(IV) perchlorate (Trimethylplatinum(IV) perchlorate tetramer)

[23411-89-4] (monomer) **$C_{12}H_{36}Cl_4O_{16}Pt_4$**



Preparative hazard

Neruda, B. *et al., J. Organomet. Chem.*, 1977, **131**, 318

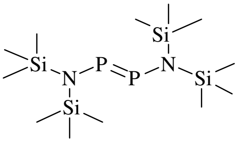
The salt is a heat and shock-sensitive explosive. Attempts to prepare it from trimethylplatinum hydroxide and perchloric acid led to violent explosions at higher acid concentrations.

See other PLATINUM COMPOUNDS

See related ALKYLMETALS, METAL PERCHLORATES

3582. Tetrakis(trimethylsilyl)diaminodiphosphene

[84521-55-1] **$C_{12}H_{36}N_2P_2$**



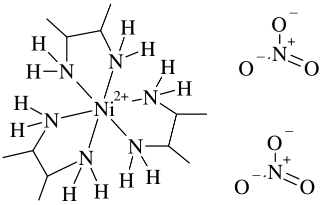
Niecke, E. *et al., Angew. Chem. (Intern. Ed.)*, 1983, **22**, 155

It is pyrophoric in air.

See related ALKYLSILANES, PHOSPHINES

3583. Tris(2,3-diaminobutane)nickel(II) nitrate

[66599-67-5] **$C_{12}H_{36}N_8NiO_6$**



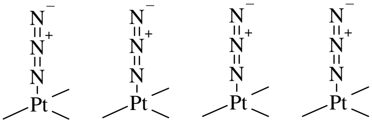
Billo, E. J. *et al., Inorg. Chim. Acta*, 1978, **26**, L10

The complex is potentially explosive.

See other AMMINEMETAL OXOSALTS

3584. Dodecamethyltetraplatinum(IV) azide (Trimethylplatinum(IV) azide tetramer)

[52732-14-6] **$C_{12}H_{36}N_{12}Pt_4$**



von Dahlen, K. H. *et al., J. Organomet. Chem.*, 1974, **65**, 267

The azide is not shock-sensitive, but detonates violently on rapid heating or exposure to flame.

Trimethyl phosphite

Neruda, B. *et al., J. Organomet. Chem.*, 1976, **111**, 241—248

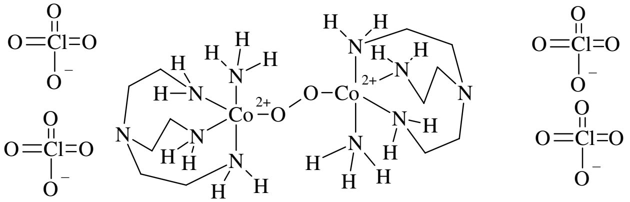
In the exothermic reaction with trimethyl phosphite to give *cis*-dimethyl-bis(trimethyl phosphito)platinum, the azide must be added to the phosphite in small portions with stirring. Addition of the phosphite to the solid azide led to a violent explosion, probably involving the transitory by-product methyl azide.

See other PLATINUM COMPOUNDS

See related METAL AZIDES

3585. *μ*-Peroxobis[ammine(2,2′,2″-triaminotriethylamine)cobalt(III)](4+) perchlorate

[37480-75-4] **$C_{12}H_{42}Cl_4Co_2N_{10}O_{18}$**



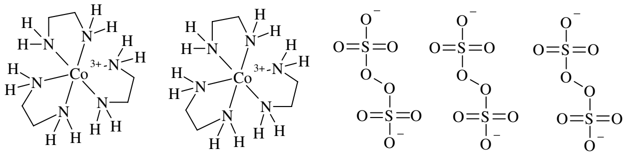
1. Yang, C.-H. *et al., Inorg. Chem.*, 1973, **12**, 666
2. Mori, M. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 619

The salt exploded at 220°C [1], and other oxosalts of this type (permanganates, possibly nitrates) are also explosive [2].

See related AMMINECHROMIUM PEROXOCOMPLEXES, AMMINEMETAL OXOSALTS

3586. Di[tris-(1,2-diaminoethane)cobalt(III)] triperoxodisulfate

[ ] **$C_{12}H_{48}Co_2N_{12}O_{24}S_6$**



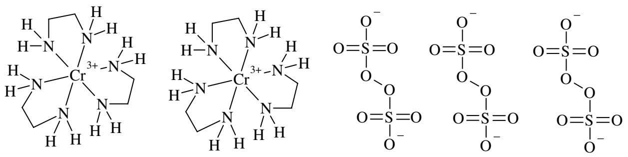
Beacom, S. E., *Nature*, 1959, **183**, 38

It explodes upon ignition, or after UV irradiation and then heating to 120°C.

See other AMMINEMETAL OXOSALTS

3587. Di[tris(1,2-diaminoethane)chromium(III)] triperoxodisulfate

[ ] **$C_{12}H_{48}Cr_2N_{12}O_{24}S_6$**



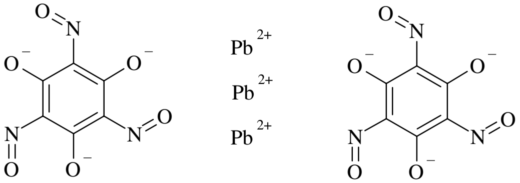
Beacom, S. E., *Nature*, 1959, **183**, 38

It explodes upon ignition, or after UV irradiation and then heating to 115°C.

See other AMMINEMETAL OXOSALTS

3588. Lead(II) trinitrosobenzene-1,3,5-trioxide

[ ] **$C_{12}N_6O_{12}Pb_3$**



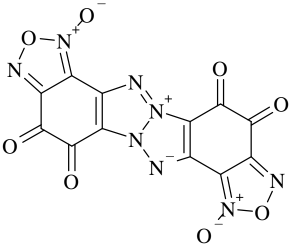
Freund, H. E., *Angew. Chem.*, 1961, **73**, 433

An air dried sample of the lead salt of trinitrosophoroglucinol exploded when disturbed, possibly owing to aerobic oxidation to the trinitro compound.

See other HEAVY METAL DERIVATIVES, NITROSO COMPOUNDS

3589a. 4,5,11,12-Tetraoxo-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3′,4′:4,5]benzotriazolo[2,1-*a*]benzotriazolo-*b*-ium 1,8-dioxide

[ ] **$C_{12}N_8O_8$**



See 5,12-Dioxo-4,4,11,11-tetrahydroxy-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3',4':4,5]benzotriazolo[2,1-*a*]benzotriazolo-*b*-ium 1,8-dioxide

See other FURAZAN *N*-OXIDES

3589b. Caesium dodecakistrifluoromethylcarba-*closo*-dodecaborate (Caesium dodeca(trifluoromethyl)carbadodecaborane(14)[1-])

[308134-22-7] **$C_{13}B_{11}CsF_6$**

$Cs^+CB_{11}(CF_3)_{12}^-$

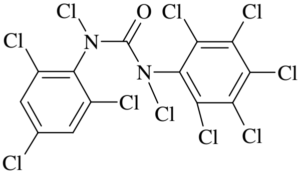
Michl, J. *et al., J. Amer. Chem. Soc.*, 2000, **122**, 10255

A friction sensitive explosive, though chemically inert, 300 mg scraped with a spatula broke glassware 2 metres distant. Explosion in oxygen definitely produces boron trifluoride and it is presumed formation of this is the driving force.

See other BORANES, METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3590. *N,N′*-dichlorobis(2,4,6-trichlorophenyl)urea

[2899-02-7] **$C_{13}H_4Cl_8N_2O$**



Ammonia

Pytlewski, L. L., *Rep. AD-A028841*, 13, Richmond (Va.), USNTIS, 1976

Contact of gaseous ammonia with the *N*-chlorourea, either alone, or mixed with zinc oxide, leads to ignition. The same could happen in contact with conc. aqueous ammonia, solid ammonium carbonate or organic amines.

Dimethyl sulfoxide

1. Pytlewski, L. L., *Rep. AD-A028841*, 13, Richmond (Va.), USNTIS, 1976
2. Owens, C. *et al., Phosphorus, Sulfur*, 1976, **2**, 177—180

Violent ignition occurs on mixing [1]. Interaction is explosive, and the products have been identified and a homolytic mechanism proposed for the reaction [2].

1-(4-Nitrophenylazo)-2-naphthol, Zinc oxide

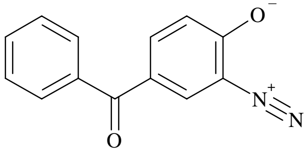
Pytlewski, L. L., *Rep. AD-A028841*, 13, Richmond (Va.), USNTIS, 1976

Spontaneous combustion in storage (occasionally at high ambient temperatures) of clothing impregnation kits containing the three title compounds was investigated. The *N*-chlorourea when heated evolves chlorine to give the isocyanate and a nitrene. Chlorine and the azo-dye react violently and serve as an initiation source of heat. Zinc oxide is converted to the chloride, which catalyses violently exothermic polymerisation of the isocyanate, the main contribution to the total very high exotherm (some 2 MJ/mol), which leads to vigorous smouldering decomposition of the whole mass, temperatures in excess of 315°C being attained. In absence of the dye, heating a mixture of the urea and zinc oxide at 5°/min leads to ignition at 130°C.

See other N-HALOGEN COMPOUNDS

3591. 5-Benzoylbenzenediazonium-2-oxide

[ ] **$C_{13}H_8N_2O_2$**

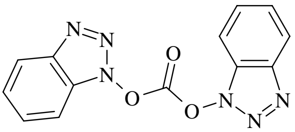


Berry, W. L., *J. Org. Chem.*, 1961, **26**, 27

Red crystals, exploding on melting (115°C). It was the highest molecular weight of several homologues to do this. Smaller compounds were often too unstable to isolate,

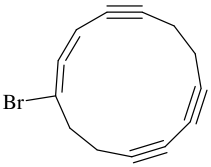
larger are not reported as exploding. Also exploding were: 5-aceto, red, 96°; 5-acetamino, orange, 120°C; 5-phenylmethyl, yellow, temperature unstated.
See other ARENEDIAZONIUM OXIDES

3592. Bis(1-benzo[*d*]triazolyl) carbonate
[88544-01-8] **$C_{13}H_8N_6O_3$**



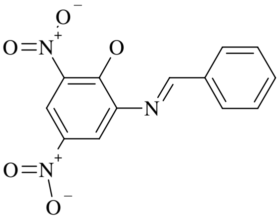
Keller, O. *et al., Chimia*, 1985, **39**(2—3), 63
It is explosive in the dry state, but if prepared at below 60°C, it may be handled wet with 30% of 1,1,2-trichloroethane.
See other HIGH-NITROGEN COMPOUNDS, N—O COMPOUNDS, TRIAZOLES

3593. 1-Bromo-1,2-cyclotridecadien-4,8,10-triyne
[17530-57-3] **$C_{13}H_9Br$**



Leznoff, C. C. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 731
It explodes at 85°C and slowly decomposes in the dark at 0°C.
See other HALOACETYLENE DERIVATIVES

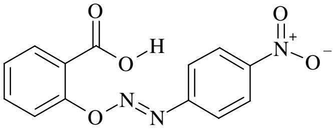
3594. 2-Benzylideneamino-4,6-dinitrophenol
[53088-06-5] **$C_{13}H_9N_3O_5$**



Metal salts
See entry 2-ARYLIDENEAMINO-4,6-DINITROPHENOL SALTS
See other POLYNITROARYL COMPOUNDS

3595. 2-(4-Nitrophenoxyazo)benzoic acid

[ ] **$C_{13}H_9N_3O_5$**



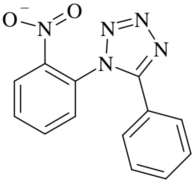
Griess, P., *Ber.*, 1884, **17**, 338

It explodes on heating.

See other ARENEDIAZOATES, N—O COMPOUNDS, ORGANIC ACIDS

3596. 1-(2-Nitrophenyl)-5-phenyltetrazole

[57761-75-8] **$C_{13}H_9N_5O_2$**



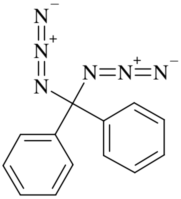
Houghton, P. G. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 771

Thermolysis of the undiluted tetrazole is violent, but controlled if dispersed in sand or in solution.

See other NITROARYL COMPOUNDS, TETRAZOLES

3597. Diazidodiphenylmethane

[17421-82-8] **$C_{13}H_{10}N_6$**



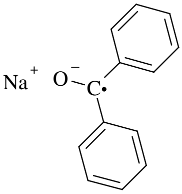
Kirchmeyer, S. et al., Synthesis, 1983, 301

Potentially explosive (a *gem*-diazide).

See other ORGANIC AZIDES

3598. Sodium diphenylketyl

[3463-17-0] **$C_{13}H_{10}NaO$**

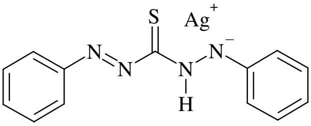


Nitrogen oxide

See Nitrogen oxide: Sodium diphenylketyl

3599. Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide

[12154-56-2] **$C_{13}H_{11}AgN_4S$**



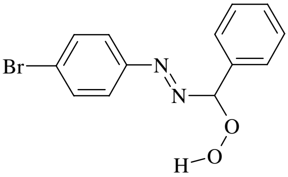
Sorbe, 1968, 126

The silver derivative of dithizone decomposes explosively at higher temperatures.

See other AZO COMPOUNDS, SILVER COMPOUNDS

3600. α-(4-Bromophenylazo)benzyl hydroperoxide

[72437-42-4] **$C_{13}H_{11}BrN_2O_2$**

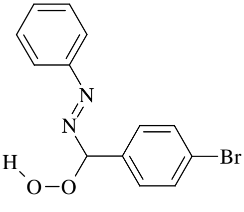


See entry α-PHENYLAZO HYDROPEROXIDES (reference 4)

See related ALKYL HYDROPEROXIDES, AZO COMPOUNDS

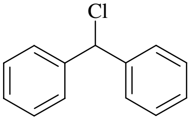
3601a. α-Phenylazo-4-bromobenzyl hydroperoxide

[83844-92-2] **$C_{13}H_{11}BrN_2O_2$**



See entry α-PHENYLAZO HYDROPEROXIDES (reference 3)
See related ALKYL HYDROPEROXIDES, AZO COMPOUNDS

3601b. Chlorodiphenylmethane (Diphenylmethyl chloride) (Benzhydryl chloride)
[90-99-3] **$C_{13}H_{11}Cl$**



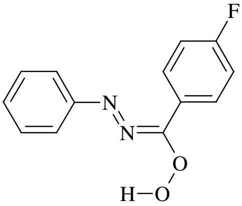
Phenol

Editor's experience

The two react vigorously on contact, with copious foaming from HCl evolution. This could be dangerous even below kilogram scale.

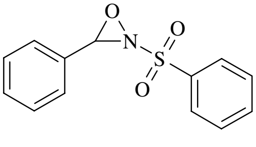
See other BENZYL COMPOUNDS

3602a. *α*-Phenylazo-4-fluorobenzyl hydroperoxide
[83844-91-1] **$C_{13}H_{11}FN_2O_2$**



See entry α-PHENYLAZO HYDROPEROXIDES (reference 3)
See related ALKYL HYDROPEROXIDES, AZO COMPOUNDS

3602b. 3-Phenyl-2-(phenylsulfonyl)oxaziridine
[63160-13-4] **$C_{13}H_{11}NO_3S$**



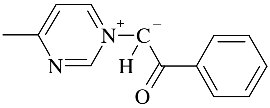
Marlatt, M. *et al., Chem. Eng. News*, 2002, **80**(8), 6

A 1 kg sample stored in a fridge decomposed, blowing off the cap and burning its container. Thermal studies show two stage exothermic decomposition, the second stage being fast and energetic. It is recommended that storage be in plastic, not glass, in smaller quantity and not for long.

See other N—O COMPOUNDS, STRAINED-RING COMPOUNDS

3602c. 4-Methylpyrimidinium benzoylmethylide (4-Methylpyrimidinium 1-(2-oxo-2-phenylethylide)

[212060-00-9] **$C_{13}H_{12}N_2O$**

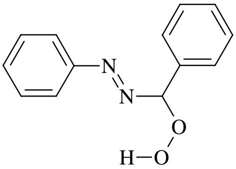


Mangalagiu, G. *et al., Eur. J. Org. Chem.*, 1999, (3), 703

This compound is described as hazardous, and also as unstable with respect to dimerisation. Analogues in which the phenyl ring has electron withdrawing substituents are stabilised, those with electron donating ones not so.

3603. α-Phenylazobenzyl hydroperoxide

[2829-31-4] **$C_{13}H_{12}N_2O_2$**



Alone, or Acids

1. Swern, 1971, Vol. 2, 19
2. Busch, M. *et al., Ber.*, 1914, **47**, 3277

The phenylhydrazones of benzaldehyde and its homologues, (or of acetone) are readily autoxidised in solution and rearrange to give the azo-hydroperoxides, isolable as solids which may explode after a short time on standing, though not on friction or impact [1]. Contact with flame or with conc. sulfuric or nitric acids also initiates explosion [2].

Phenylhydrazine

Bergman, M. *et al., Ber.*, 1923, **56**, 681

The hydroperoxide reacts violently after warming for a few min. with phenylhydrazine.

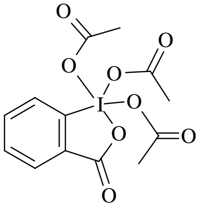
See entry α PHENYLAZO HYDROPEROXIDES

See other REDOX REACTIONS

See related ALKYL HYDROPEROXIDES, AZO COMPOUNDS

3604. 1,1,1-Triacetoxy-1,2-benziodoxol-3-one

[87413-09-0] **$C_{13}H_{13}IO_8$**



Plumb, J. B., *Chem. Eng. News*, 1990, **68**(29), 3

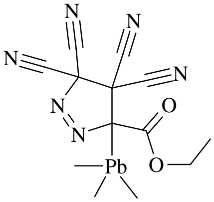
The title compound is produced by treatment of 2-iodylbenzoic acid with acetic anhydride in acetic acid, and has found wide application as a mild oxidant ('Dess-Martin periodinane') for 1y and 2y alcohols. Although it appears not to be sensitive to impact, unlike the precursor acid, both explode violently when heated under confinement. The oxidant, on treatment with water is hydrolysed back to the explosive 2-iodylbenzoic acid. Forethought and caution are advised before using these explosive materials on any scale of working.

See 2-Iodylbenzoic acid

See other IODINE COMPOUNDS, OXIDANTS

3605. 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,5-dihydro-3*H*-pyrazole

[52762-90-0] **$C_{13}H_{14}N_6O_2Pb$**



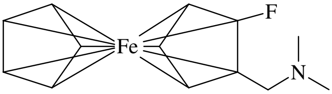
Houben-Weyl, 1975, Vl. 13.3, 221

It tends to explode on heating.

See related ALKYLMETALS, CYANO COMPOUNDS

3606. 2-(Dimethylaminomethyl)fluoroferrocene

[54747-08-9] **$C_{13}H_{16}FFeN$**



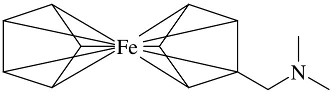
Preparative hazard

See Perchloryl fluoride: 2-Lithio(dimethylaminomethyl)ferrocene

See other ORGANOMETALLICS

3607. Dimethylaminomethylferrocene

[1271-86-9] **$C_{13}H_{17}FeN$**



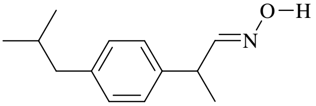
Nitric acid, Water

See Nitric acid: Dimethylaminomethylferrocene, etc.

See other ORGANOMETALLICS

3608. 2-Methyl-2-[4-(2-methylpropyl)phenyl]oximinoethane (*p*-Isobutylphenyl-α-methylacetaldehyde oxime)

[58609-72-6] **$C_{13}H_{19}NO$**



P. Cardillo, P., 1992, Personal Communication

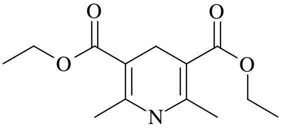
On the first full-scale run of a modified process for the nickel catalysed isomerisation of the oxime to the corresponding amide, on 1200 kg scale in toluene solution under reflux in place of the previous water, the reaction overheated (to > 180°C), pressurised, and then escaped confinement. Investigation showed the explosion to be purely a runaway reaction caused by a slower start than previously. It was recommended that the oxime be charged in portions, and the solvent changed to the higher-boiling xylene.

See other OXIMES

See related ALDEHYDES

3609. Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate

[1149-23-1] **$C_{13}H_{19}NO_4$**

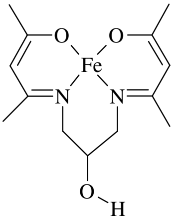


4-Nitropyridine *N*-oxide

See 4-Nitropyridine *N*-oxide: Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate

3610. Iron(II) chelate of bis-*N,N*-(2-pentanon-4-ylidene)-1,3-diamino-2-hydroxypropane

[22281-49-8] **$C_{13}H_{20}FeN_2O_3$**



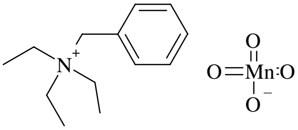
Berenbaum, M. B., US Pat. 3 388 141, 1968

The solid chelate is pyrophoric in air, burning to iron(III) oxide.

See other PYROPHORIC MATERIALS

3611a. Benzyltriethylammonium permanganate

[68844-25-7] **$C_{13}H_{22}MnNO_4$**



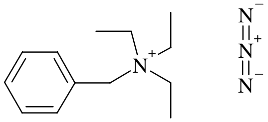
1. Schmidt, H.-J. *et al. Angew. Chem. (Intern. Ed.)*, 1979, **18**, 69
2. Jäger, H. *et al., Angew. Chem. (Intern. Ed.)*, 1979, **18**, 786—787
3. Schmidt, H.-J. *et al., Angew. Chem. (Intern. Ed.)*, 1979, **18**, 787
4. Leddy, B. P. *et al., Tetrahedron Lett.*, 1980, **21**, 2261—2262
5. *See entry* SELF-ACCELERATING REACTIONS
6. Graefe, J. *et al., Angew. Chem. (Intern. Ed.)*, 1983, **23**, 625

The quaternary oxosalt, previously reported as insensitive to hammer-blows or heating to 100°C for 5 min. [1], exploded violently during vacuum drying at 80°C/ 1.3 mbar. Detailed work has shown that it explodes at 120°C when heated at 4°/ min, or at above 50° after various induction periods, e.g. 14 h/60°, 90 min/80°, 25, 28 min/90°, 7 min/100°C [2]. It is also sensitive to heavy blows [2,3]. It explodes in a m.p. capillary at 80—90°C, but may be stabilised by absorption on alumina [4]. An induction period of 80 h/60°C has also been reported [5]. In a further laboratory accident, material dried for 36 h at only 20°C under high vacuum ignited during transfer from a flask to another container, generating flames 1 m long. Since it undergoes violent decomposition in the absence of heating, extreme care and precautions are obviously necessary. It appears that drying conditions may be critical [5].

See other INDUCTION PERIOD INCIDENTS, QUATERNARY OXIDANTS

3611b. Benzyltriethylammonium azide

[ ] **$C_{13}H_{22}N_4$**



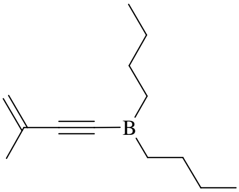
www2.umdnj.edu/eohssweb/aiha/accidents/explosion. 2002, American Industrial Hygiene Association.

A preparation on less than 10 g scale was isolated by removal of solvent on a rotary evaporator. As the flask was raised from the water bath, but before any attempt was made to remove the flask from the evaporator or break the vacuum, the material detonated, causing permanent injury to the experimenter. This represents greater sensitivity then might be anticipated with the ‘sandbagging’ given by the bulky cation.

See other ORGANIC AZIDES

3612a. Dibutyl-3-methyl-3-buten-1-ynlborane

[ ] **$C_{13}H_{23}B$**



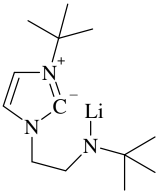
Davidsohn, W. E., *Chem. Rev.*, 1967, **67**, 75

It ignites in air.

See other ACETYLENIC COMPOUNDS, ALKYLBORANES

3612b. 1-*tert*-Butyl-3-(*N*-*tert*-butyl-2-lithaminoethyl)imidazol-2-ylidene

[ ] **$C_{13}H_{24}LiN_3$**



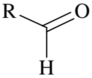
Mungur, S. A. *et al., Chem. Comm.*, 2004, (23), 2738

This trapped carbene (which actually exists as a dimer with tetra-coordinated Li atoms) smokes on exposure to air and also on grinding with fluorocarbon solvent, from which it seems able to remove fluoride.

See also METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3613. Tridecanal

[ ] **$C_{13}H_{26}O$**



1. Steele, A. B. *et al., Chem. Engrg.*, 1959, **66**(4), 160
2. Urben, P. G., private comm., 1989

Reported to ignite in air [1]. This is typical of medium-range aldehydes, particularly if exposure is increased by sorption on paper or cloth, ignition often occurring within 2 hours [2].

See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

3614. Tris(trimethylsilyl)aluminium etherate ([1,1′-Oxybis[ethane]]tris(trimethyl silyl)aluminium)

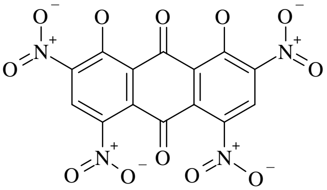
[75441-10-0] **$C_{13}H_{37}AlOSi_3$**

$(Me_3Si)_3Al.OEt_2$

Avery, M. A. *et al., J. Amer. Chem. Soc.*, 1992, **114**(3), 974
This compound was pyrophoric even as a relatively dilute pentane solution (Editor's Note: This was a crude preparation probably containing many other organometallics).
See Tris(trimethylsilyl)aluminium
See other ALKYLMETALS, ALKYLSILANES

3615. 1,8-Dihydroxy-2,4,5,7-tetranitroanthraquinone

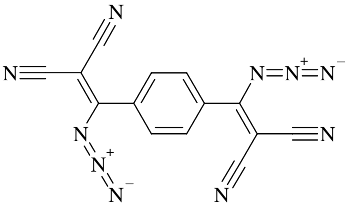
[ ] **$C_{14}H_4N_4O_{12}$**



Sorbe, 1968, 153
It is explosive.
See other POLYNITROARYL COMPOUNDS

3616. 2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile)

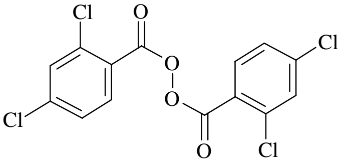
[ ] **$C_{14}H_4N_{10}$**



Moore, J. A., *et al., Macromolecules*, 1993, **26**(5), 916
It exploded when filtered on a sinter, destroying the apparatus.
See related BENZYL COMPOUNDS, CYANO COMPOUNDS, ORGANIC AZIDES

3617a. Bis(2,4-dichlorobenzoyl) peroxide

[133-14-2] **$C_{14}H_6Cl_4O_4$**



‘Lucidol Data Sheet’, Buffalo, Wallace & Tiernan, 1963

Whereas the pure compound is extremely shock-sensitive and decomposes rapidly at 80°C, the commercial 50% dispersion in plasticiser is not shock-sensitive.

Charcoal

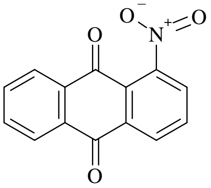
Leleu, *Cahiers*, 1980, (99), 279

A mixture with a solution of the peroxide in a dialkyl phthalate plasticiser decomposes exothermically but moderately, (probably catalysed by trace heavy metals in the carbon).

See other COMMERCIAL ORGANIC PEROXIDES, DIACYL PEROXIDES

3617b. 1-Nitroanthraquinone

[82-34-8] **$C_{14}H_7NO_4$**



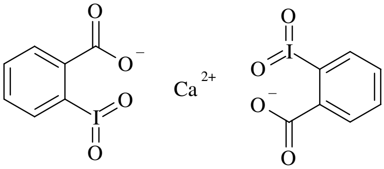
MARS Database, 1998, short report 007

A runaway decomposition in a melting vessel associated with distillation of the crude product burst the vessel and led to a major fire. The short report does not include detailed circumstances. The decomposition was attributed to the catalytic effects of impurities. However, it seems that nitric acid was also present.

See Nitric acid: most sub-entries

3618. Calcium 2-iodylbenzoate

[59643-77-5] **$C_{14}H_8CaI_2O_8$**



1. Unpublished information, 1948
2. Merck, 1976, 55

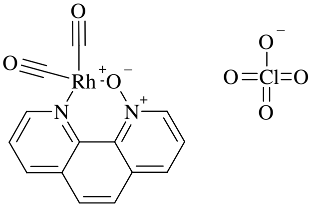
Formulated granules accidentally dried to below normal moisture content exploded violently [1]. The ammonium salt is similarly unstable to heating [2].

See 2-Iodylbenzoic acid

See other IODINE COMPOUNDS

3619. Dicarbonyl(phenanthroline *N*-oxide)rhodium(I) perchlorate

[84578-90-5] **$C_{14}H_8ClN_2O_7Rh$**



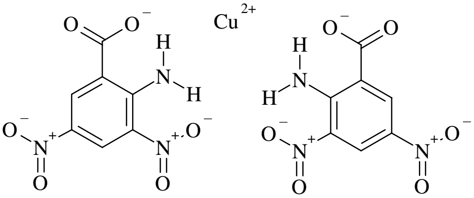
Uson, R. *et al., J. Organomet. Chem.*, 1982, **240**, 433, footnote f

It exploded violently during microanalytical combustion.

See related AMMINEMETAL OXOSALTS

3620. Copper(II) 3,5-dinitroanthranilate

[58302-41-3] **$C_{14}H_8CuN_6O_{12}$**

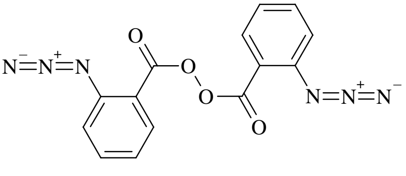


See Silver 3,5-dinitroanthranilate

See other POLYNITROARYL COMPOUNDS

3621. Bis(2-azidobenzoyl) peroxide

[20442-99-3] **$C_{14}H_8N_6O_4$**



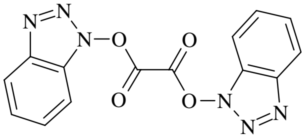
1. Leffler, J. E., *Chem. Eng. News*, 1963, **41**(48), 45
2. Hoffman, J., *Chem. Eng. News*, 1963, **41**(52), 5

A small sample of crystalline material on a sintered glass funnel detonated with extreme violence when touched with a metal spatula [1]. Static electrical initiation may have been involved [2].

See related DIACYL PEROXIDES, ORGANIC AZIDES, STATIC INITIATION INCIDENTS

3622. Bis(1-benzo[*d*]triazolyl) oxalate

[89028-37-5] **$C_{14}H_8N_6O_4$**



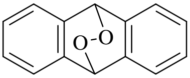
Keller, O. *et al., Chimia*, 1985, **39**(2—3), 63

It is explosive in the dry state, but if prepared at below 50°C, it may be handled wet with 40% of 1,1,2-trichloroethane.

See other HIGH-NITROGEN COMPOUNDS, N—O COMPOUNDS, TRIAZOLES

3623. 9,10-Epidioxyanthracene

[220-42-8] **$C_{14}H_8O_2$**



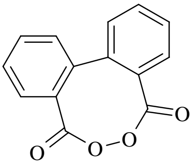
Dufraisse, C. *et al., Compt. rend.*, 1935, **201**, 428

It decomposes explosively at 120°C.

See other CYCLIC PEROXIDES

3624. 2,2-Biphenyldicarbonyl peroxide (Dibenzo-*d,f*-1,2-dioxocin-3,8-dione)

[6109-04-2] **$C_{14}H_8O_4$**



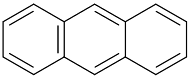
Ramirez, F., *J. Amer. Chem. Soc.*, 1964, **86**, 4394

It explodes violently on heating to 70°C or on impact, but can be preserved at low temperature.

See other CYCLIC PEROXIDES, DIACYL PEROXIDES

3625. Anthracene

[120-12-7] **$C_{14}H_{10}$**

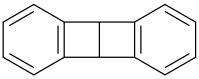


HCS 1980, 159

Fluorine
See Fluorine: Hydrocarbons

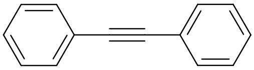
Other reactants
Yoshida, 1980, 35
MRH values calculated for 13 combinations with oxidants are given.

3626. 2,3:5,6-Dibenzobicyclo[3.3.0]hexane (9,10 Dewar anthracene)
[79403-75-1] **$C_{14}H_{10}$**



Pritschins, W. *et al., Tetrahedron Lett.*, 1982, **23**, 1153
It reverts violently to anthracene at 73°C in a tube sealed under argon.
See other STRAINED-RING COMPOUNDS

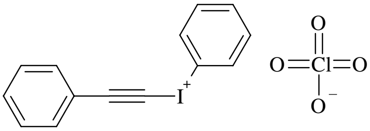
3627. Diphenylethyne (Diphenylacetylene)
[501-65-5] **$C_{14}H_{10}$**



Aluminium chloride, Nitrobenzene
1. Eisch, J. J. *et al., Chem. Eng. News*, 1998, **76**(6), 2
2. Eisch, J. J., Personal communication, 1998.

On adding one drop of nitrobenzene to an equimolar, ten millimolar, mixture of the other two solids a violent reaction produced gas and carbonaceous material. This was initially attributed to the oxidative powers of the nitrobenzene [1]. However, diphenylacetylene is a high energy molecule, ΔH_f° + 315 kJ/mole. At least 98% of the potential chemical energy present will have been the diphenylacetylene. It is probable that the nitrobenzene merely provided a liquid phase in which the aluminium chloride could interact with the acetylene, catalysing reaction beyond the intended azulene dimerisation product [2].
See other ACETYLENIC COMPOUNDS

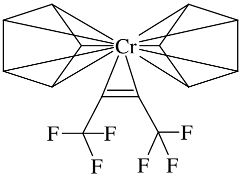
3628. Phenyl,phenylethynyliodonium perchlorate
[126208-50-2] **$C_{14}H_{10}ClIO_4$**



Stang, P. J., *Chem. Eng. News*, **68**(34), 2
This salt is explosive, which was attributed to the iodonium group.
See other ACETYLENIC COMPOUNDS, IODINE COMPOUNDS, NON-METAL PERCHLORATES

3629. Bis(cyclopentadienyl)hexafluoro-2-butynechromium

[63618-84-8] **$C_{14}H_{10}CrF_6$**



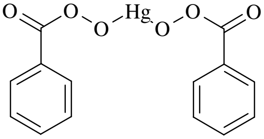
Chisholm, M. H. *et al., Synth. React. Inorg. Metal-Org. Chem.*, 1977, **7**, 283

This adduct of chromocene with hexafluoro-2-butyne decomposes after a few mins. at ambient temperature, either under nitrogen or vacuum. The process is autocatalytic and violently exothermic, several explosions having occurred.

See other ACETYLENIC COMPOUNDS, ORGANOMETALLICS

3630. Mercury(II) peroxybenzoate

[18918-17-7] **$C_{14}H_{10}HgO_6$**



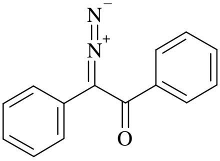
Castrantas, 1965, 19

It explodes if heated above its normal decomposition temperature of 100—110°C.

See other MERCURY COMPOUNDS, PEROXOACID SALTS

3631. 1-Benzoyl-1-phenyldiazomethane

[3469-17-8] **$C_{14}H_{10}N_2O$**



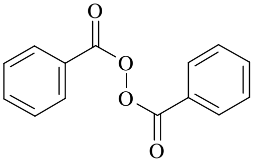
Nenitzescu, C. D. *et al., Org. Synth.*, 1943, Coll. Vol. 2, 497

The material may explode if heated to above 40°C.

See other DIAZO COMPOUNDS

3632. Dibenzoyl peroxide

[94-36-0] **$C_{14}H_{10}O_4$**



(*MCA SD-81*, 1960); *FPA H56*, 1977; *HCS 1980*, 196 (both latter relate to commercial material dispersed in water or plasticiser)

1. *MCA SD-81*, 1960
2. Lappin, G. R., *Chem. Eng. News*, 1948, **26**, 3518
3. Taub, D., *Chem. Eng. News*, 1949, **27**, 46
4. Nametkin, S. S., *Chem. Abs.*, 1931, **25**, 4127_8
5. Nozaki, K. *et al., J. Amer. Chem. Soc.*, 1946, **68**, 1692
6. Fine, D. J. *et al., Combust. Flame*, 1967, **11**, 71—78
7. McCloskey, C. M. *et al., Chem. Abs.*, 1967, **66**, 12613c
8. Uetake, K. *et al., Chem. Abs.*, 1974, **81**, 5175
9. Sekida, O., Jap. Pat. 40 220, 1974
10. Anon., *Sichere Chemiearb.*, 1976, **28**, 49
11. Anon., *Jahresber.*, 1980, 66

The dry material is readily ignited, burns very rapidly and is moderately sensitive to heat, shock, friction or contact with combustible materials. When heated above its m.p. (103—105°C), instantaneous and explosive decomposition occurs without flame, but the decomposition products are flammable. If under confinement (or in large bulk), decomposition may be violently explosive [1]. An explosion which occurred when a screw-capped bottle of the peroxide was opened was attributed to friction initiating a mixture of peroxide and organic dust in the cap threads [2]. Waxed paper tubs are recommended to store this and other sensitive solids [3]. Crystallisation of the peroxide from hot chloroform solution involves a high risk of explosion. Precipitation from cold chloroform solution by methanol is safer [4]. Water- or plasticiser-containing pastes of dibenzoyl peroxide are much safer for industrial use.

The explosive decomposition of the solid has been studied in detail [6]. The effect of moisture upon ignitibility and explosive behaviour under confinement was studied. A moisture content of 3% allowed slow burning only, and at 5% ignition did not occur [7]. Thermal instability was studied using a pressure vessel test, ignition delay time, TGA and DSC, and decomposition products were identified [8]. The presence of acyl chlorides renders dibenzoyl peroxide impact-sensitive [9]. There is a further report of a violent explosion during purification of the peroxide by Soxhlet extraction with hot chloroform [10]. Residual traces of the peroxide in a polythene feed pipe exploded when it was cut with a handsaw [11]. The heat of decomposition has been determined as 1.39 kJ/g. The calculated value of 69°C for critical ignition temperature coincides with that previously recorded.

See also Picric acid

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

Aniline

Bailey, P. S. *et al., J. Chem. Educ.*, 1975, **52**, 525

Addition of a drop of aniline to 1 g of the peroxide leads to mildly explosive decomposition after a short delay.

N-Bromosuccinimide, 4-Toluic acid

See N-Bromosuccinimide: Dibenzoyl peroxide, etc.

Carbon tetrachloride, Ethylene

Bolt, R. O. *et al., Chem. Eng. News*, 1947, **25**, 1866

Interaction of ethylene and carbon tetrachloride at elevated temperatures and pressures, initiated with benzoyl peroxide as radical source, caused violent explosions on several occasions. Recommended precautions include use of minimum pressure and quantity of initiator, maximum agitation, and presence of water as an inert moderator of high specific heat.

See Ethylene: Carbon tetrachloride

Charcoal

Leleu, *Cahiers*, 1980, (99), 279

At 50°C, a mixture reacts violently, evolving white fumes. (Catalytic decomposition by traces of heavy metals in the charcoal seems likely to be involved.)

Dimethyl sulfide

Pryor, W. A. *et al., J. Org. Chem.*, 1972, **37**, 2885

The rapid decomposition of benzoyl peroxide by dimethyl sulfide is explosive in absence of solvent.

N,N-Dimethylaniline

Horner, L. *et al., Chem. Ber.*, 1953, **86**, 1071—1072

The solid peroxide exploded on contact with a drop of dimethylaniline.

Lithium tetrahydroaluminate MRH 4.39/15

Sutton, D. A., *Chem. & Ind.*, 1951, 272

One or two attempts to reduce the diacyl peroxide in ether led to a moderately violent explosion.

See other REDOX REACTIONS

Methyl methacrylate

MCA Case History No. 996

Local overheating and ignition occurred when solid benzoyl peroxide was put into a beaker which had been rinsed out with methyl methacrylate. Contact between the peroxide, a powerful oxidant and radical source, and oxidisable or polymerisable materials should only be under controlled conditions.

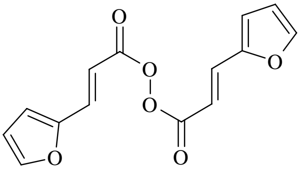
Vinyl acetate

See Vinyl acetate: Dibenzoyl peroxide, etc.

See other DIACYL PEROXIDES

3633. Bis-3-(2-furyl)acryloyl peroxide

[22978-89-8] **$C_{14}H_{10}O_6$**



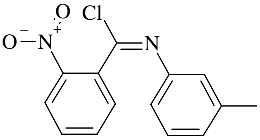
Milas, N. A. *et al., J. Amer. Chem. Soc.*, 1934, **56**, 1219

It explodes violently on heating.

See other DIACYL PEROXIDES

3634. *N*-(3-Methylphenyl)-2-nitrobenzimidyl chloride

[ ] **$C_{14}H_{11}ClN_2O_2$**

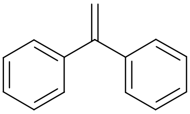


Preparative hazard

See Phosphorus pentachloride: 3’-Methyl-2-nitrobenzanilide

3635. 1,1-Diphenylethylene

[530-48-3] **$C_{14}H_{12}$**



Oxygen

Staudinger, H., *Ber.*, 1925, **58**, 1075

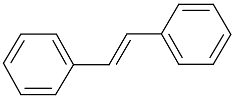
Exposure of the alkene to oxygen at ambient temperature and pressure produces an alkene—oxygen interpolymeric peroxide which explodes lightly on heating. An attempt to react the alkene with oxygen at 100 bar and 40—50°C caused a violent explosion in the autoclave.

See other POLYPEROXIDES

See related ALKENES

3636. *trans*-1,2-Diphenylethylene (Stilbene)

[103-30-0] **$C_{14}H_{12}$**



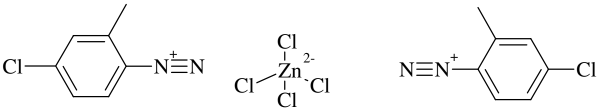
It is mildly endothermic (ΔH_f° (s) +135.4 kJ/mol, 0.75 kJ/g), and the *cis*- isomer [645-49-8] will be rather more so.

See other ENDOTHERMIC COMPOUNDS

See related ALKENES

3637. 5-Chlorotoluene-2-diazonium tetrachlorozincate

[89453-69-0] **$C_{14}H_{12}Cl_6N_4Zn$**



Anon., *ABCM Quart Safety Summ.*, 1953, **24**, 42

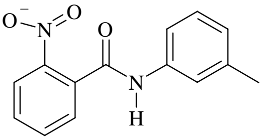
A batch containing only half the normal water content (60%) exploded violently during ball-milling. Tests later showed the dry material to be shock-sensitive.

See Benzenediazonium tetrachlorozincate

See other DIAZONIUM SALTS

3638. 3′-Methyl-2-nitrobenzanilide

[50623-64-8] **$C_{14}H_{12}N_2O_3$**



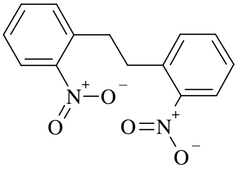
Phosphorus pentachloride

See Phosphorus pentachloride: 3’-Methyl-2-nitrobenzanilide

See other NITROARYL COMPOUNDS

3639. 1,2-Bis(2-nitrophenyl)ethane (2,2’-Dinitrobibenzyl)

[16968-19-7] **$C_{14}H_{12}N_2O_4$**

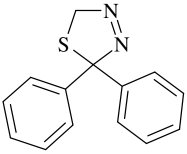


Preparative hazard

See 2-Nitrotoluene: Alkali

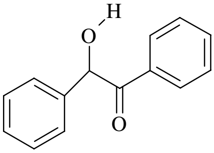
See other POLYNITROARYL COMPOUNDS

3640a. 2,2-Diphenyl-1,3,4-thiadiazoline
[79999-60-3] **$C_{14}H_{12}N_2S$**



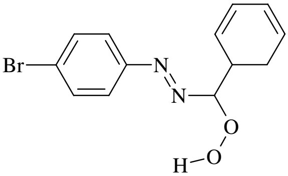
Kolwinsch, I. *et al., J. Amer. Chem. Soc.*, 1981, **103**, 7032
The crystalline solid isolated at —78°C suddenly decomposed with nitrogen evolution at —20°C.
See related AZO COMPOUNDS, N—S COMPOUNDS

3640b. 2-Hydroxy-1,2-diphenylethanone (2-Hydroxy-2-phenylacetophenone) (Benzoin)
[119-53-9] **$C_{14}H_{12}O_2$**



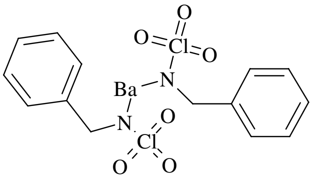
Preparative hazard
See PHASE CHANGES

3641. α-(4-Bromophenylazo)phenylethyl α-hydroperoxide
[91364-94-2] **$C_{14}H_{13}BrN_2O_2$**



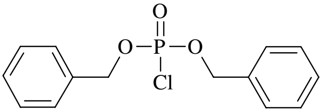
See entry αPHENYLAZO HYDROPEROXIDES (reference 4)
See related ALKYL HYDROPEROXIDES, AZO COMPOUNDS

3642. Barium *N*-perchlorylbenzylamide
[89521-42-6] **$C_{14}H_{14}BaCl_2N_2O_6$**



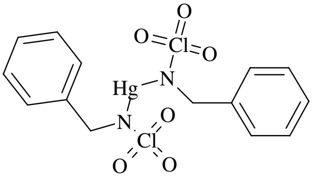
It explodes on impact.
See entry PERCHLORYLAMIDE SALTS (reference 2)
See other BENZYL COMPOUNDS, N-METAL DERIVATIVES

3643. Dibenzyl phosphorochloridate ('Dibenzyl chlorophosphate')
[538-37-4] **$C_{14}H_{14}ClO_3P$**



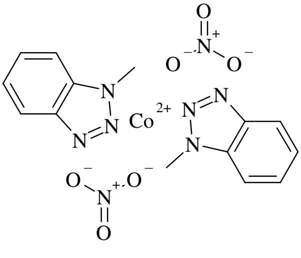
Atherton, F. R. *et al., J. Chem. Soc.*, 1945, 382
It is too unstable to be distilled, and the precursory phosphite also tends to decompose on distillation.
See Dibenzyl phosphite
See other BENZYL COMPOUNDS, PHOSPHORUS ESTERS

3644. Mercury(II) *N*-perchlorylbenzylamide
[89521-44-8] **$C_{14}H_{14}Cl_2HgN_2O_6$**



It explodes on impact, or on heating above 120°C.
See entry PERCHLORYLAMIDE SALTS (reference 2)
See other BENZYL COMPOUNDS, MERCURY COMPOUNDS, N-METAL DERIVATIVES

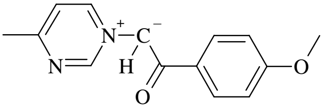
3645a. Bis(1-methylbenzotriazole)cobalt(II) nitrate
[123668-66-6] **$C_{14}H_{14}CoN_8O_6$**



Zafiropoulos, T. F. *et al., Monatsh.*, 1989, **120**(4), 357
Explodes at 260 C.
See other AMMINEMETAL NITRATES, TRIAZOLES

3645b. 4-Methylpyrimidinium 4-methoxybenzoylmethylide (4-Methylpyrimidinium 1-(2-oxo-2-(4-methoxyphenyl)ethylide))

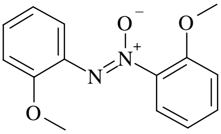
[212060-03-2] **$C_{14}H_{14}N_2O_2$**



See 4-Methylpyrimidinium benzoylmethylide

3646a. 2-Azoxyanisole

[13620-57-0] **$C_{14}H_{14}N_2O_3$**



Preparative hazard

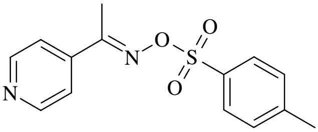
See 2-Nitroanisole: Sodium hydroxide, etc.

See related AZO COMPOUNDS

3646b. 4-[1-(4-Methylbenzenesulfonyloximino)ethyl]pyridine (4-Acetopyridine oxime *O-para*-toluenesulfonate)

[107445-22-1] *E*-isomer [74209-51-1] 3-pyridyl isomer

$C_{14}H_{14}N_2O_3S$



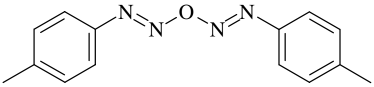
Brown Ripin, D. H. *et al., Chem. Eng. News*, 2001, **79**(40) 8

The three isomeric acetopyridine oxime tosylates, intermediates in an Organic Syntheses procedure wherein they are thermally rearranged, were found to have heats of decomposition around 1 kJ/g, enough to present a serious hazard if the reaction be conducted much beyond the decagram scale. Onset of decomposition is quite sudden at around 80°C. They are also marginally shock sensitive. The acetophenone homologue has a much lower heat of decomposition around 0.4 kJ/g.

See other OXIMES

3647a. Bis(toluenediazo) oxide (1,1-Oxybis(4-methylphenyldiazene))

[90238-04-3] **$C_{14}H_{14}N_4O$**



Alone, or Toluene

Bamberger, E., *Ber.*, 1896, **39**, 452, 458

Extremely unstable, it explodes under its reaction liquor at above —4°C. Very shock- and friction-sensitive, a small sample exploded when dried on a porous tile and set off the moist material some distance away. Contact with toluene, even at —5°C, causes an explosive reaction with flame.

See other BIS(ARENEDIAZO) OXIDES

3647b. Di(2-aminobenzoyl) hydrazide (Anthranoyl hydrazide)

[43100-30-7] $H_2NC_6H_4CONHNHCOC_6H_4NH_2$

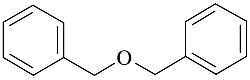
$H_2NC_6H_4CONHNHCOC_6H_4NH_2$

Phosphorus tribromide

See Phosphorus tribromide, Hydrazine derivatives

3648. Dibenzyl ether

[103-50-4] $C_{14}H_{14}O$



HCS 1980, 204

Aluminium dichloride hydride

See Aluminium dichloride hydride diethyl etherate

Other reactants

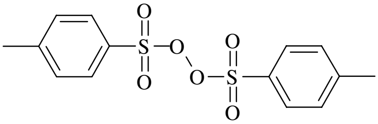
Yoshida, 1980, 330

MRH values calculated for 13 combinations with oxidants are given.

See other BENZYL COMPOUNDS, PEROXIDISABLE COMPOUNDS

3649. Di-4-toluenesulfonyl peroxide

[1886-68-6] $C_{14}H_{14}O_6S_2$



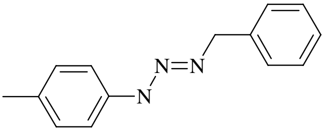
1. Bolte, J. *et al., Tetrahedron Lett.*, 1965, **6**, 1929
2. Dannley, R. L. *et al., J. Org. Chem.*, 1966, **31**, 154

The peroxide was too unstable to dry thoroughly [1]; such samples often exploded spontaneously [2].

See other DIACYL PEROXIDES

3650. 1-Benzyl-3-(4-tolyl)triazene

[17683-09-9] **$C_{14}H_{15}N_3$**



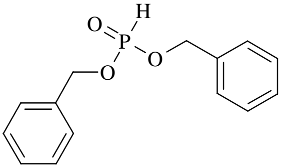
White, E. H. *et al., Org. Synth.*, 1973, Coll. Vol. 5, 799

Vacuum sublimation at 90—100°C led to a violent explosion.

See other BENZYL COMPOUNDS, TRIAZENES

3651. Dibenzyl phosphite

[17176-77-1] **$C_{14}H_{15}O_3P$**



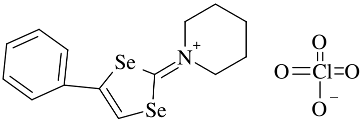
Atherton, F. R. *et al., J. Chem. Soc.*, 1945, 382; 1948, 1106

It decomposes at 160°C, but prolonged heating at 120°C may have the same effect. Not more than 50 g should be distilled at one time, using high-vacuum conditions (b.p 100—120°C/0.001 mbar) unless a preliminary treatment to remove acidic impurities has been used.

See other BENZYL COMPOUNDS, PHOSPHORUS ESTERS

3652. 1-(4-Phenyl-1,3-diselenolylidene)piperidinium perchlorate

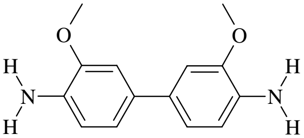
[53808-76-7] **$C_{14}H_{16}ClNO_4Se_2$**



See entry 1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES

3653. 3,3′-Dimethoxy-4,4′-diaminobiphenyl (*o*-Dianisidine)

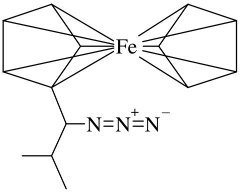
[119-90-4] **$C_{14}H_{16}N_2O_2$**



The finely powdered carcinogen is a significant dust explosion hazard.

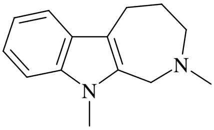
See entry DUST EXPLOSION INCIDENTS (reference 22)
See other ORGANIC BASES

3654. 1-Ferrocenyl-2-methylpropyl azide
[105017-95-6] **$C_{14}H_{17}FeN_3$**



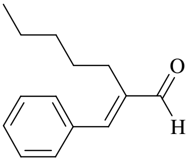
Cushman, M. *et al., J. Org. Chem.*, 1987, **52**, 1517—1521
Heating the title azide at 100°C caused explosive decomposition.
See related ORGANIC AZIDES, ORGANOMETALLICS

3655. 2,10-Dimethyl-1,2,3,4,5,10-hexahydroazepino[3-4,*b*]indole
[75142-81-3] **$C_{14}H_{18}N_2$**



4-Chlorobenzenesulfonyl azide
See 4-Chlorobenzenesulfonyl azide: 2,10-Dimethyl-1,2,3,4 ...

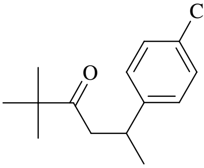
3656. *α*-Pentylcinnamaldehyde (3-Phenyl-2-pentylpropenal)
[122-40-7] **$C_{14}H_{18}O$**



Anon., *Chem. Trade. J.*, 1937, **100**, 362
This is very prone to spontaneous oxidative heating. A mixture with absorbent cotton attained a temperature of 230°C 4 min after exposure to air.
See other ALDEHYDES, PEROXIDISABLE COMPOUNDS

3657a. 5-*p*-Chlorophenyl-2,2-dimethyl-3-hexanone (5-(4-chlorophenyl)-2,2-dimethyl-3-hexanone)

[55058-76-9] **$C_{14}H_{19}ClO$**

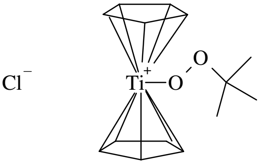


Peroxyacetic acid

See Peroxyacetic acid: 5-*p*-Chlorophenyl-2,2-dimethyl-3-hexanone

3657b. *tert*-Butylperoxydicyclopentadienyltitanium chloride

[48231-42-6] **$C_{14}H_{19}ClO_2Ti$**



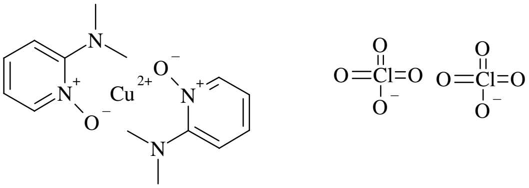
DiPasquale, A. G. *et al., J. Amer. Chem. Soc.*, 2002, **124**(49), 14534

It can be explosive in the solid state and should be handled carefully

See other ORGANOMETALLIC PEROXIDES

3658. Bis(2-dimethylaminopyridine N-oxide)copper(II) perchlorate (Bis(*N,N*-dimethyl-2-pyridinamine-1-oxide)copper(2+) perchlorate)

[67157-99-7] **$C_{14}H_{20}Cl_2CuN_4O_{10}$**



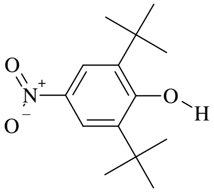
West, D. X., *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 155—159

It decomposes explosively at 270°C without prior weight loss.

See related AMMINEMETAL OXOSALTS

3659. 2,6-Di-*tert*-butyl-4-nitrophenol

[728-40-5] **$C_{14}H_{21}NO_3$**



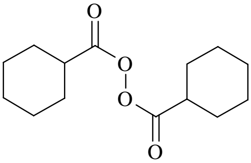
1. *ASESB Expl. Incid. Rept.*, 1961, 24
2. Barnes, T. J. *et al., J. Chem. Soc.*, 1961, 953

A sample of the compound exploded violently after short heating to 100°C. Although this was attributed to presence of polynitro derivatives [1], the thermal decomposition of this type of nitro compound is known [2].

See other NITROARYL COMPOUNDS

3660. Dicyclohexylcarbonyl peroxide

[4904-55-6] **$C_{14}H_{22}O_4$**



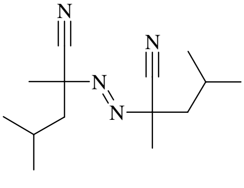
Castrantas, 1965, 17

Large quantities may explode without apparent reason.

See other DIACYL PEROXIDES

3661. 2,2′-Azobis(2,4-dimethylvaleronitrile)

[4419-11-8] **$C_{14}H_{24}N_4$**



Yoshida, T., private comm., 1984

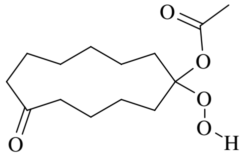
The low-melting solid of limited thermal stability (max. safe storage temperature 20°C, self-heating decomposition detected above 30°C) will explode on heavy impact (150 kgcm), but is of low sensitivity to ignition. However, 3 cases of spontaneous decomposition in storage or transportation have been noted.

See entry BLOWING AGENTS

See other AZO COMPOUNDS, CYANO COMPOUNDS

3662. 1-Acetoxy-1-hydroperoxy-6-cyclodecanone

[ ] $C_{14}H_{24}O_5$



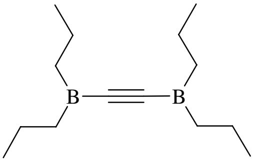
Criegee, R. *et al., Ann.*, 1949, **564**, 9

It explodes on removal from a freezing mixture.

See other 1-OXYPEROXY COMPOUNDS

3663. Bis(dipropylborino)acetylene

[ ] $C_{14}H_{28}B_2$



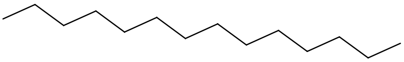
Hartmann, H. *et al., Z. Anorg. Allgem. Chem.*, 1959, **299**, 179

Both n- and iso-propyl derivatives ignite in air.

See other ACETYLENIC COMPOUNDS, ALKYLBORANES

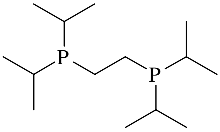
†3664. Tetradecane

[629-59-4] $C_{14}H_{30}$



3665. Acetylenebis(triethyllead)

[5120-07-0] $C_{14}H_{30}Pb_2$



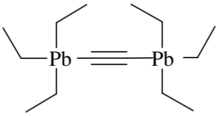
Beerman, C. *et al., Z. Anorg. Chem.*, 1954, **276**, 20

It is very sensitive to heat, oxygen or light, and should not be dried.

See related ALKYLMETALS, METAL ACETYLIDES

3666. Acetylenebis(triethyltin)

[994-99-0] **$C_{14}H_{30}Sn_2$**



Stannic chloride

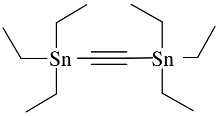
Beerman, C. *et al., Z. Anorg. Chem.*, 1954, **276**, 20

The product of interaction is highly explosive.

See related ALKYLMETALS, METAL ACETYLIDES

3667. 1,2-Bis-(di-2-propylphosphino)ethane

[87532-69-2] **$C_{14}H_{32}P_2$**



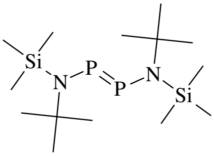
Benn, R. *et al., Z. Naturforsch. B*, 1986, **41**B, 680—691

The title ligand, and the bis(*tert*-butylphosphino) lower homologue are pyrophoric in air.

See related ALKYLPHOSPHINES

3668. *N,N′*-Di-*tert*-butyl-*N,N′*-bis(trimethylsilyl)diaminophosphene

[85923-32-6] **$C_{14}H_{36}N_2P_2Si_2$**



Niecke, E. *et al., Angew. Chem. (Intern. Ed.)*, 1983, **22**, 486

Highly pyrophoric, like the tetrakis(trimethylsilyl) analogue.

See related ALKYLSILANES, PHOSPHINES

3669. Heptakis(dimethylamino)trialuminium triboron pentahydride

[28016-59-3] **$C_{14}H_{47}Al_3B_3N_7$**

[2808]

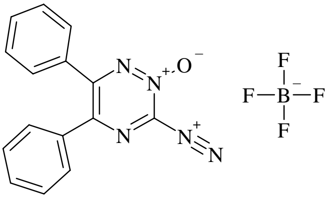
Hall, R. E., *et al., Inorg. Chem.*, 1969, **8**, 270

The crystalline solid ignites in air.

See other COMPLEX HYDRIDES

See related BORANES

3670. 5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide
[98571-91-6] **$C_{15}H_{10}BF_4N_5O$**

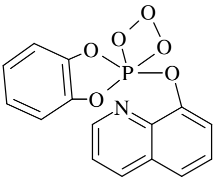


Jovanovic, V., *Heterocycles*, 1985, **23**, 1969—1981

The isolated diazonium salt exploded when exposed to air, and also on impact.

See other DIAZONIUM TETRAHALOBORATES, HIGH-NITROGEN COMPOUNDS, N-OXIDES

3671. Pyrocatecholato(2-)(quinolin-8-olato-*N,O*)-trioxygenido(2-)phosphorus
[82434-14-8] **$C_{15}H_{10}NO_6P$**



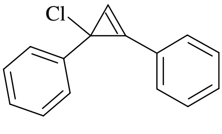
Koenig, M. *et al., Tetrahedron Lett.*, 1982, **23**, 422

The hexavalent phosphorus ozonide, stable at —20°C, exploded in contact with air or on warming to ambient temperature.

See other OZONIDES

See related PHOSPHORUS ESTERS

3672. 3-Chloro-1,3-diphenylcyclopropene
[20421-00-5] **$C_{15}H_{11}Cl$**



Preparative hazard

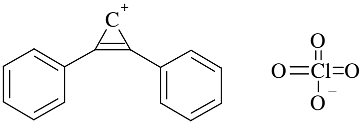
Padwa, A. *et al., J. Org. Chem.*, 1969, **34**, 2732

If the crude title product (from interaction of 3-chloro-3-phenyldiaziridine and diphenylacetylene) is not purified immediately after preparation, violent decomposition occurs.

See other STRAINED-RING COMPOUNDS

3673. Diphenylcyclopropenylium perchlorate

[37647-36-2] **$C_{15}H_{11}ClO_4$**



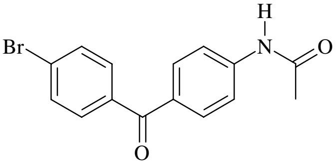
Hughes, R. P. *et al., Organometallics*, 1985, **4,** 1761—1766

It should not be air dried, and as an explosive salt it must be handled with care.

See other NON-METAL PERCHLORATES

3674. 4(4′-Bromobenzoyl)acetanilide

[ ] **$C_{15}H_{12}BrNO_2$**

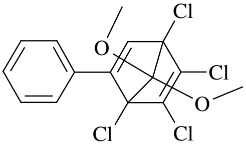


Dimethyl sulfoxide

See Dimethyl sulfoxide: 4(4’-Bromobenzoyl)acetanilide

3675. 1,2,3,4-Tetrachloro-7,7-dimethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene

[15584-65-3] **$C_{15}H_{12}Cl_4O_2$**

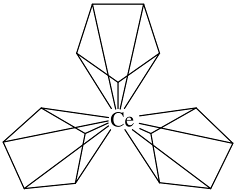


Hoffmann, R. W. *et al., Tetrahedron*, 1965, **21**, 900

Pyrolysis of the material at 130°C under nitrogen at low pressure to give tetramethoxyethylene may be explosive if more than 25 g is used.

3676. Tris(cyclopentadienyl)cerium

[1298-53-9] **$C_{15}H_{15}Ce$**



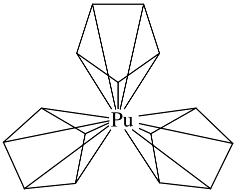
Preparative hazard

See Sodium nitrate: Tris(cyclopentadienyl)cerium

See other ORGANOMETALLICS

3677. Tris(cyclopentadienyl)plutonium

[12216-08-9] **$C_{15}H_{15}Pu$**



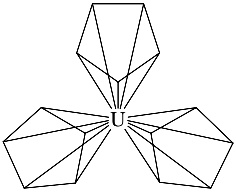
Bailar, 1973, Vol. 5, 407

It ignites in air.

See other ORGANOMETALLICS

3678. Tris(cyclopentadienyl)uranium

[54007-00-0] **$C_{15}H_{15}U$**



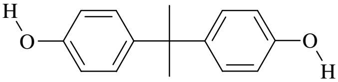
Bailar, 1973, Vol. 5, 407

It ignites in air.

See other ORGANOMETALLICS

3679. 2,2-Bis(4-hydroxyphenyl)propane

[80-05-7] **$C_{15}H_{16}O_2$**

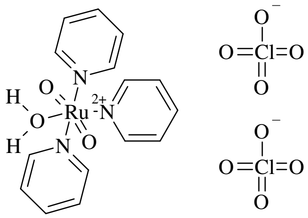


The finely powdered resin component (Bisphenol-A) is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

3680. *trans*-Aquadioxo(terpyridine)ruthenium(2+) diperchlorate

[ ] **$C_{15}H_{17}Cl_2N_5O_{10}Ru$**



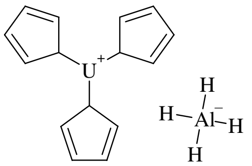
Meyer, T. J. *et al., Inorg. Chem.*, 1992, **31**(8), 1375

The complex sometimes explodes when scraped against a glass frit with a metal spatula.

See other AMMINEMETAL OXOSALTS

3681. Tricyclopentadienyluranium tetrahydroaluminate

[107633-87-4] **$C_{15}H_{19}AlU$**



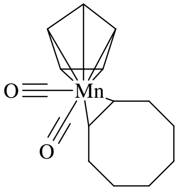
Ossola, S. *et al., J. Organomet. Chem.*, 1986, **310**(1), C1

It ignites in air, and reacts with benzene, dimethoxyethane, THF and toluene.

See related COMPLEX HYDRIDES, HEAVY METAL DERIVATIVES, ORGANOMETALLICS, PYROPHORIC MATERIALS

3682. *cis*-Dicarbonyl(cyclopentadienyl)cyclooctenemanganese

[49716-47-4] **$C_{15}H_{19}MnO_2$**



Butler, I. S. *et al., J. Inorg. Nucl. Chem.*, 1978, **40**, 1937

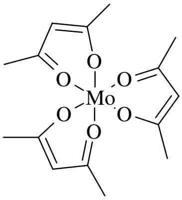
Overheating during high-vacuum sublimation may produce pyrophoric manganese which explodes on opening the sublimer to atmosphere.

See PYROPHORIC METALS

See other ORGANOMETALLICS

3683. Tris(2,4-pentanedionato)molybdenum(III)

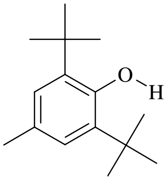
[14284-90-3] **$C_{15}H_{21}MoO_6$**



Larson. M. L. *et al., Inorg. Synth.*, 1966, **8**, 153
It rapidly oxidises in air, sometimes igniting.
See related ORGANOMETALLICS

3684. 2,6-Di-*tert*-butyl-4-cresol

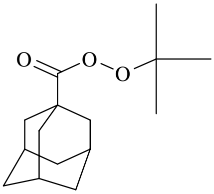
[128-37-0] **$C_{15}H_{24}O$**



The finely powdered anti-oxidant is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

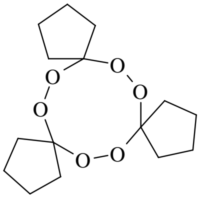
3685. *tert*-Butyl 1-adamantaneperoxycarboxylate

[21245-43-2] **$C_{15}H_{24}O_3$**



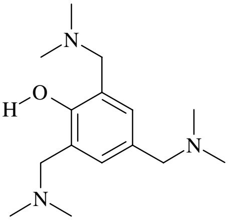
Razuvajev, G. A. *et al., Tetrahedron*, 1969, **25**, 4925
It explodes on heating to 90—100°C.
See other PEROXYESTERS

3686. Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane
[4884-18-8] **$C_{15}H_{24}O_6$**



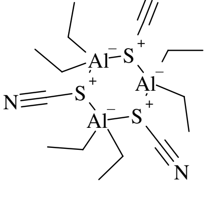
Bjorklund, G. H. *et al., Trans. R. Soc. Can. (Sect. III)*, 1950, **44**, 25
A violent explosive, very sensitive to shock, friction and rapid heating.
See Hydrogen peroxide: Ketones, etc.
See other CYCLIC PEROXIDES

3687. 2,4,6-Tris(dimethylaminomethyl)phenol
[90-72-2] **$C_{15}H_{27}N_3O$**



Cellulose nitrate
See CELLULOSE NITRATE: Amines
See other ORGANIC BASES

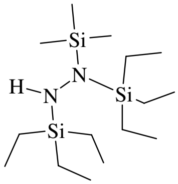
3688. Hexaethyltrialuminium trithiocyanate
[17548-36-6] **$C_{15}H_{30}Al_3N_3S_3$**



Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 947
On heating at 210° under vacuum it disproportionates explosively, but smoothly at180°C.
See related ALKYLALUMINIUM HALIDES, METAL CYANATES

3689a. 1,2-Bis(triethylsilyl)trimethylsilylhydrazine

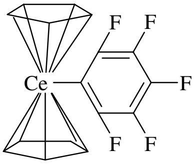
[13272-04-3] **$C_{15}H_{40}N_2Si_3$**



See entry SILYLHYDRAZINES
See related ALKYLSILANES

3689b. Dicyclopentadienylpentafluorophenylcerium

[ ] **$C_{16}H_{10}CeF_5$**



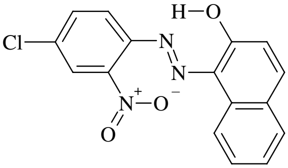
Maron, L. *et al., J. Amer. Chem. Soc.*, 2005, **127**(1), 279

This compound, a reaction intermediate known to decompose slowly to dicyclopentadienylcerium fluoride and tetrafluorobenzyne, decomposed violently in a sealed capillary tube at about 125°C during attempted melting point determination.

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3690. 1-(4-Chloro-2-nitrobenzeneazo)-2-hydroxynaphthalene

[6410-13-5] **$C_{16}H_{10}ClN_3O_3$**

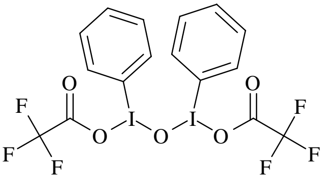


Lead chromate

See Lead chromate: Azo-dyestuffs
See other AZO COMPOUNDS

3691. μ-Oxo-*I,I*-bis(trifluoroacetato-*O*)-*I,I*-diphenyldiodine(III)

[91879-79-7] **$C_{16}H_{10}F_6I_2O_5$**



Boutin, R. H. *et al., J. Org. Chem.*, 1984, **49**, 4278, 4284

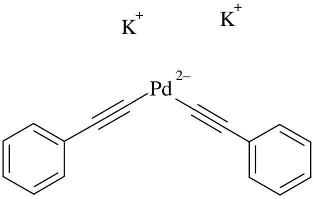
It detonated at 220°C during determination of the m.p.

See [*I,I*-Bis(trifluoroacetoxy)iodo]benzene

See other IODINE COMPOUNDS

3692. Potassium bis(phenylethynyl)palladate(2−)

[66986-75-2] **$C_{16}H_{10}K_2Pd$**



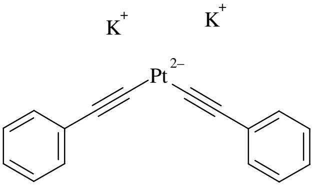
Air, or Water

Immediately pyrophoric in air, and explosive decomposition occurs with aqueous reagents; the sodium salt is similar.

See entry COMPLEX ACETYLIDES (reference 2)

3693. Potassium bis(phenylethynyl)platinate(2−)

[ ] **$C_{16}H_{10}K_2Pt$**



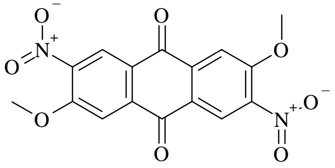
Air, or Water

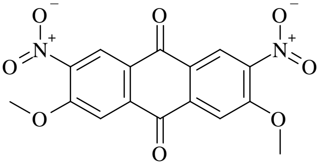
Immediately pyrophoric in air, and explosive decomposition occurs with water; the sodium salt is similar.

See entry COMPLEX ACETYLIDES (reference 2)

3694. *mixo*-Dimethoxydinitroanthraquinone

[6407-56-3] (1,5,4,8-) [53939-55-2] (1,8:4,5-) **$C_{16}H_{10}N_2O_8$**





Oleum

White, D. L. *et al.*, Ger. Offen. 2 451 569, 1975

In an alternative method of preparing *mixo*-dihydroxyanthraquinonedisulfonic acid by heating the title compound with oleum to effect simultaneous hydrolysis, denitration and sulfonation of the nucleus, there is the possibility of formation of methyl nitrate from the scission fragments.

See other POLYNITROARYL COMPOUNDS

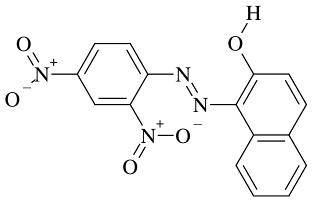
Sulfuric acid

Hildreth, J. D., *Chem. & Ind.*, 1970, 1592

During hydrolysis of crude dimethoxy compound by heating in sulfuric acid, a runaway exothermic decomposition occurred causing vessel failure. Experiment showed a threshold decomposition temperature of 150—155°C, and an oxidising effect of the nitro groups, yielding CO and CO_2 above 162°C.

3695. 1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene (Pigment orange 5)

[3468-63-1] **$C_{16}H_{10}N_4O_5$**



The solid deflagrates at 1.8 cm/min.

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 3)

See other DEFLAGRATION INCIDENTS

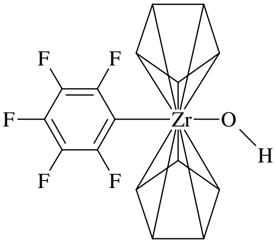
Lead chromate

See Lead chromate: Azo-dyestuffs

See other AZO COMPOUNDS, POLYNITROARYL COMPOUNDS

3696. Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide

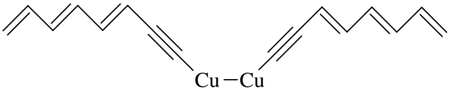
[ ] **$C_{16}H_{11}F_5OZr$**



Chaudhari, M. A. *et al., J. Chem. Soc. A*, 1966, 840
Decomposition on heating in air above 260°C is sometimes explosive.
See other ORGANOMETALLICS
See related HALO-ARYLMETALS

3697. Copper 1,3,5-octatrien-7-ynide

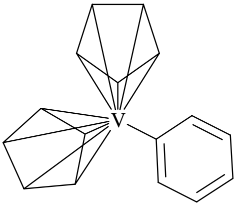
[ ] **$C_{16}H_{14}Cu_2$**



Georgieff, K. K. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 5495
It deflagrates on heating in air.
See other METAL ACETYLIDES

3698. Bis(cyclopentadienyl)phenylvanadium

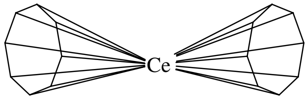
[12212-56-5] **$C_{16}H_{15}V$**



Gibson, 1969, 178
It ignites in air.
See other ORGANOMETALLICS
See related ARYLMETALS

3699. Bis(cyclooctatetraenyl)cerium (Bis(η^8-1,3,5,7-cyclooctatetraene)cerium)

[37205-27-9] **$C_{16}H_{16}Ce$**



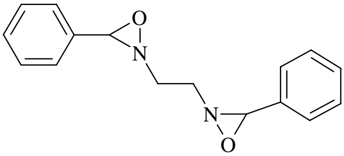
Edelmann, F. T. *et al., Angew. Chem. (Int.),* 1994, **33**(15/16) 1618

This sandwich compound, nominally the Ce(IV) derivative of cyclooctatetraene(2-) is highly pyrophoric.

See other ORGANOMETALLICS

3700. 2,2′-(1,2-Ethylenebis)3-phenyloxaziridine

[54222-34-3] **$C_{16}H_{16}N_2O_2$**



MCA Case History No. 2175

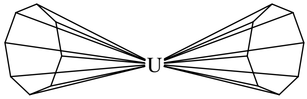
The washed crude product from oxidation of 1,2-dibenzylideneaminoethane in methylene chloride solution exploded violently during vacuum evaporation at a relatively low temperature.

See 2,2’-Di-*tert*-butyl-3,3’-bioxaziridine

See other N—O COMPOUNDS, STRAINED-RING COMPOUNDS

3701. Bis(cycloctatetraene)uranium(0)

[11079-26-8] **$C_{16}H_{16}U$**



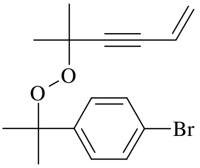
Streitweiser, A. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 7364

It inflames in air.

See other ORGANOMETALLICS

3703. 2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide

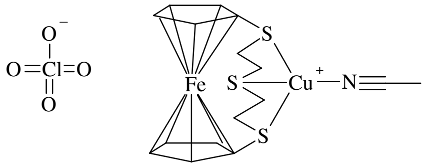
[88519-63-5] **$C_{16}H_{19}BrO_2$**



See 2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide (below)
See other ACETYLENIC PEROXIDES, DIALKYL PEROXIDES

3704. 1,4,7-Trithia[7]ferrocenophene—acetonitrilecopper(I) perchlorate

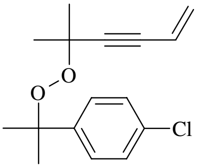
[110725-79-6] **$C_{16}H_{19}ClCuFe_2NO_4S_3$**



Sato, M. *et al., Bull. Chem. Soc. Japan*, 1986, **59**, 3611—3615
It exploded on heating.
See other AMMINEMETAL OXOSALTS, NON-METAL PERCHLORATES

3705a. 2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide

[ ] **$C_{16}H_{19}ClO_2$**



Vilenskaya, M. R. *et al., Zh. Org. Khim., 1981,* **17**, 959—961
The acetylenic peroxide and its bromo analogue explode at 120—130°C.
See other ACETYLENIC PEROXIDES, DIALKYL PEROXIDES

3705b. Bis(2,6-Dimethoxyphenyl)hydroxyselenonium perchlorate

[231279-29-1] **$[MeO)_2C_6H_3]_2Se^+OHClO_4$**

$[MeO)_2C_6H_3]_2Se^+OHClO_4$

Wada, M. *et. al., J. Organomet. Chem.*, 1999, **580**(2) 282
This compound , the perchloric acid adduct of the selenoxide, exploded at 139°C during melting point determination. The tellurium analogue was similar.
See also 3998 Perchloric acid, Sulfoxides

3705c. Bis(2,6-Dimethoxyphenyl)hydroxytelluronium perchlorate

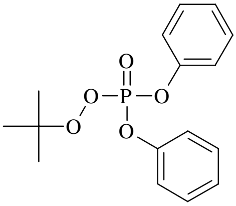
[231279-31-5] **$[MeO)_2C_6H_3]_2Te^+OHClO_4^-$**

$[MeO)_2C_6H_3]_2Te^+OHClO_4^-$

See above

3706. *O—O-tert*-Butyl diphenyl monoperoxophosphate

[20194-03-0] **$C_{16}H_{19}O_5P$**



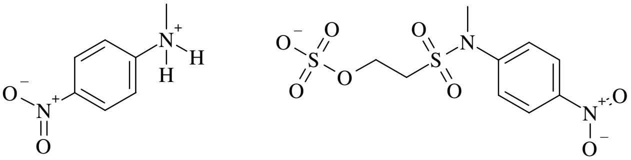
Rieche, A. *et al., Chem. Ber.*, 1962, **95**, 385

The material deflagrated as a solid, or decomposed exothermically in its reaction mixture soon after preparation.

See other tert-BUTYL PEROXOPHOSPHATE DERIVATIVES, PHOSPHORUS ESTERS

3707. *N*-Methyl-4-nitroanilinium 2-[*N*-methyl-*N*-(4-nitrophenyl)aminosulfonyl]-ethylsulfate

[ ] **$C_{16}H_{20}N_4O_{10}S_2$**



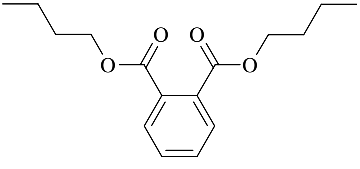
There is a preparative hazard for this reaction product of *N*-methyl-*p*-nitroaniline and ‘carbyl sulfate’.

See 2,4-Dithia-1,3-dioxane-2,2,4,4-tetraoxide: *N*-Methyl-4-nitroaniline, etc.

See related NITROARYL COMPOUNDS, SULFUR ESTERS

3708. Dibutyl phthalate

[84-74-2] **$C_{16}H_{22}O_4$**

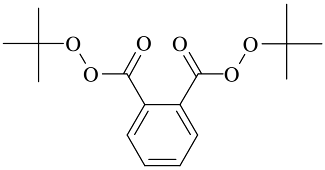


Chlorine

See Chlorine: Dibutyl phthalate

3709. Di-*tert*-butyl diperoxyphthalate

[2155-71-7] **$C_{16}H_{22}O_6$**



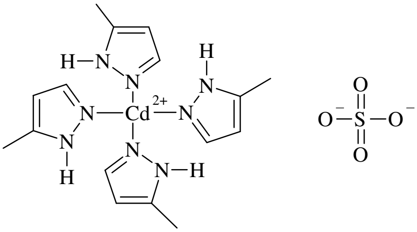
Castrantas, 1965, 17

It is shock-sensitive.

See other PEROXYESTERS

3710. Tetrakis(3-methylpyrazole)cadmium sulfate

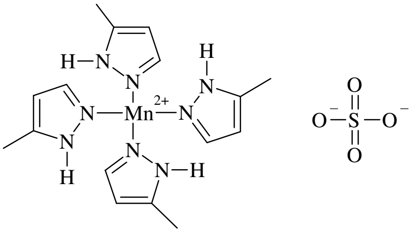
[55060-82-7] **$C_{16}H_{24}CdN_8O_4S$**



See entry AMMINEMETAL OXOSALTS (reference 9)

3711a. Tetrakis(3-methylpyrazole)manganese(II) sulfate

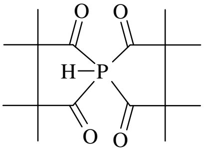
[55060-79-2] **$C_{16}H_{24}MnN_8O_4S$**



See entry AMMINEMETAL OXOSALTS (reference 9)

3711b. 2,2,3,3,7,7,8,8-Octamethyl-1,4,6,9-tetraoxo-5-phosphaspiro [4.4] nonane

[ ] **$C_{16}H_{25}PO_4$**



Haire, D. L. *et al., Magn. Reson. Chem.*, 1999, **37**(11), 767
This compound was found to decompose violently on heating above 160°C.
See also ALKYL PHOSPHINES

3712. Bis-*O,N*[(*N'*-pent-2-en-2-oxy-4-ylidene)-*N,S*-dimethyldithiocarbazate]copper(II) perchlorate

[ ] **$C_{16}H_{28}Cl_2CuN_4O_{10}S_4$**

$[MeSC(S)N(Me)N=C(Me)CH=C(Me)O]_2Cu\ (HClO_4)_2$

Preparative hazard

Akbar Ali, M. *et al., J. Inorg. Nucl. Chem.*, 1978, **40**, 452
Attempts to prepare this and the corresponding *S*-benzyl complex gave highly explosive products. It appears that the ligand hydrolysed and that the bis(*N,S*-dialkyldithiocarbazate)copper perchlorates were obtained and it was these which exploded.
See related AMMINEMETAL OXOSALTS

3713. Potassium bis(8-(4-nitrophenylthio)undecahydrodicarbaundecaborato)cobaltate(1-)

[155147-44-7] **$C_{16}H_{28}B_{18}CoKN_2O_4S_2$**

$(O_2NC_6H_4SC_2B_9H_{10})_2Co^-K^+$

Knyazev, S. P. *et al., Chem. Abs.*, 1994, **120** 298911d
Nitro compounds of this series are reported as exploding on grinding or on rapid heating to >200°C. The equivalent ferrate and a mono(2-nitrophenyl) substituted bisboratocobaltate were also prepared.
See other BORANES

3714. Potassium bis(8-(4-nitrophenylthio)undecahydrodicarbaundecaborato)ferrate(1-)

[155147-41-4] **$C_{16}H_{28}B_{18}FeKN_2O_4S_2$**

$(O_2NC_6H_4SC_2B_9H_{10})_2Fe^-K^+$

See Potassium bis(8-(4-nitrophenylthio)undecahydrodicarbaundecaborato)cobaltate(1-)
See other BORANES

3715. Bis (2-phenyl-1,2-dicarbadodecaborane(12)-1-yl)diazene) (1,1'Azo-2-phenyl-1,2-dicarbadodecaborane(14))

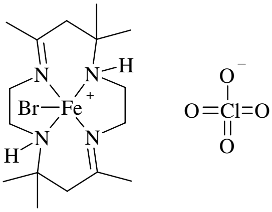
[73399-75-4] **$C_{16}H_{30}B_{20}N_2$**

[2839]

See entry AZOCARBABORANES

3716. Bromo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclo-tetradecadieneiron(II) perchlorate

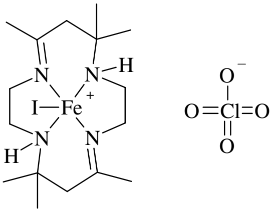
[31122-43-7] **$C_{16}H_{32}BrClFeN_4O_4$**



See entry [14] DIENE-N_4 COMPLEXES

3717. Iodo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate

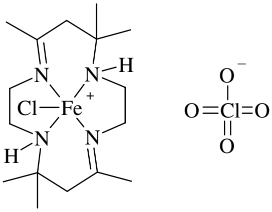
[31122-35-7] **$C_{16}H_{32}ClFeIN_4O_4$**



See entry [14] DIENE-N_4 COMPLEXES

3718. Chloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate

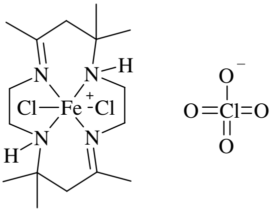
[31122-42-6] **$C_{16}H_{32}Cl_2FeN_4O_4$**



See entry [14] DIENE-N_4 COMPLEXES

3719. Dichloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(III) perchlorate

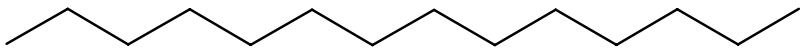
[36691-97-1] **$C_{16}H_{32}Cl_3FeN_4O_4$**



See entry [14] DIENE-N_4 COMPLEXES

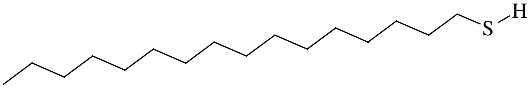
†3720. Hexadecane

[544-76-3] **$C_{16}H_{34}$**



3721. Hexadecanethiol

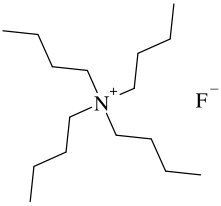
[2917-26-2] **$C_{16}H_{34}S$**



Nitric acid
See Nitric acid: Alkanethiols

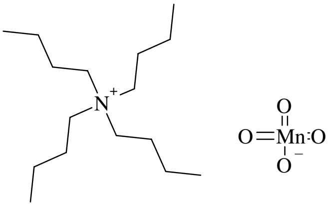
3722. Tetrabutylammonium fluoride

[429-41-4] **$C_{16}H_{36}FN$**



Hexamethyldisilazane, Pyridine *N*-oxide
See Pyridine *N*-oxide: Hexamethyldisilazane, etc.

3723. Tetrabutylammonium permanganate
[35638-41-6] **$C_{16}H_{36}MnNO_4$**

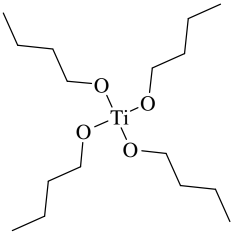


1. Sala, T. *et al., J. Chem. Soc., Chem. Comm.*, 1978, 254
2. Morris, J. A. *et al., Chem. & Ind.*, 1978, 446

Portions of a 20 g sample of the oxidant salt, prepared exactly as the published description [1], had been used uneventfully during a few days. Subsequently, as a 2 g portion was tipped out onto glazed paper, it ignited and burned violently, leading also to ignition of the bottled material [2].

See other QUATERNARY OXIDANTS

3724. Titanium butoxide
[5593-70-4] **$C_{16}H_{36}O_6Ti$**



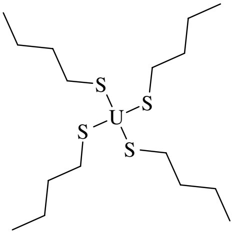
HCS 1980, 884

Ethyl terephthalate, Ethylene glycol

See Dimethyl terephthalate: Ethylene glycol, Titanium butoxide

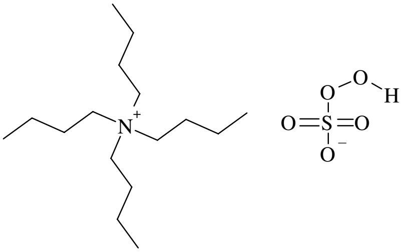
See other METAL ALKOXIDES

3725. Tetrakis(butylthio)uranium
[ ] **$C_{16}H_{36}S_4U$**



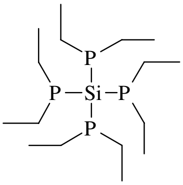
Bailar, 1973, Vol. 5, 416
It ignites in air.
See related METAL ALKOXIDES, METAL SULFIDES

3726. Tetrabutylammonium hydrogen monoperoxysulfate
[104548-30-3] **$C_{16}H_{37}NO_5S$**



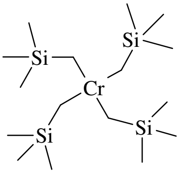
Trost, B. M. *et al., J. Org. Chem.*, 1987, **53**, 532—537
Although no instability was noted, and a small sample was insensitive to a hammer blow, it should be treated as potentially unstable as an organic oxidant.
See other QUATERNARY OXIDANTS

3727a. Tetrakis(diethylphosphino)silane
[ ] **$C_{16}H_{40}P_4Si$**



Air, or Water
Fritz, G. *et al., Angew. Chem. (Intern. Ed.)*, 1963, **2**, 262
It ignites in air and is extremely sensitive to water.
See related ALKYLPHOSPHINES, ALKYLSILANES

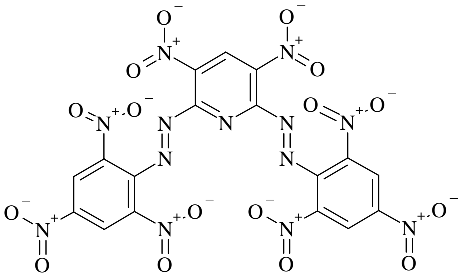
3727b. Tetrakis(trimethylsilylmethyl)chromium
[35304-18-4] **$C_{16}H_{44}CrSi_4$**



See Tetrakis(2,2-dimethylpropyl)chromium

3728. 2,6-Bis(picrylazo)-3,5-dinitropyridine

[55106-96-2] **$C_{17}H_5N_{13}O_{16}$**

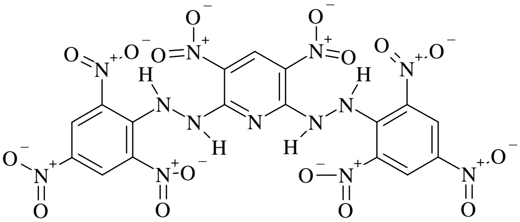


Explosive.

See entry POLYNITROAZOPYRIDINES

3729. 2,6-Bis(2-picrylhydrazino)-3,5-dinitropyridine

[55106-95-1] **$C_{17}H_9N_{13}O_{16}$**

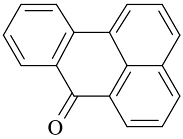


Explosive.

See entry POLYNITROAZOPYRIDINES

3730. Benzanthrone

[82-05-3] **$C_{17}H_{10}O$**

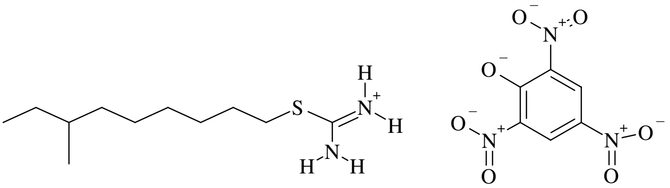


Nitrobenzene, Potassium hydroxide

See Nitrobenzene: Alkali (reference 4)

3731a. *S*-7-Methylnonylthiouronium picrate

[ ] **$C_{17}H_{27}N_5O_7S$**



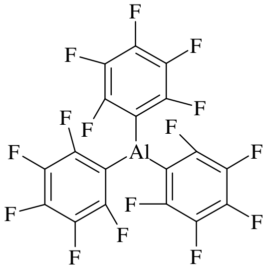
Leese, C. L. *et al. J. Chem. Soc.*, 1950, 2739

The salt explodes if heated rapidly.

See other PICRATES

3731b. Tris(pentafluorophenyl)aluminium (Tris(pentafluorophenyl)alane)

[168704-96-9] **$C_{18}AlF_{16}$**



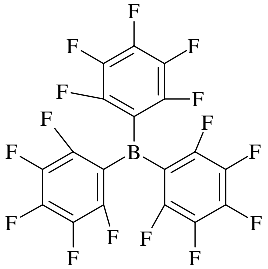
Feng, S. *et al., Organometallics*, 2002, **21**(5), 832

The unsolvated compound should be handled carefully since it is sensitive to both heat and shock.

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3732. Tris(pentafluorophenyl)boron

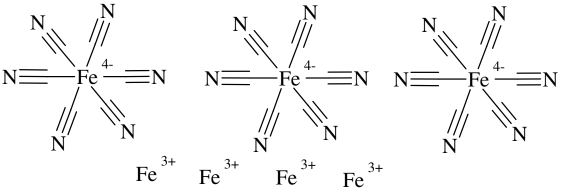
[1109-15-5] **$C_{18}BF_{15}$**



See Triethylaluminium: Tris(pentafluorophenyl)boron

See also METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3733a. Iron(III) hexacyanoferrate(4—)
[14038-43-8] **$C_{18}Fe_7N_{18}$**



Widmann, G. *et al., Thermochim. Acta*, 1988, **134**, 451—455

The energy of decomposition of Prussian blue in air in the range 210—360°C was determined by DSC as 2.42 kJ/g, peaking at 271°C. When nitrogen was used as inerting gas in the sealed micro-crucible, decomposition was delayed to 250—350°C with a broad peak.

Blown castor oil, Turkey red oil (sulfonated castor oil)

Gärtner, K., *Farben-Ztg.*, 1938, **43**, 1118

A colour mixture containing the 3 components ignited spontaneously. Oxidation products in the air-blown oil may have reacted exothermally with the complex cyanide, a reducant.

Ethylene oxide

1. Wagle, N. G., *Chem. Brit.*, 1977, **13**, 317
2. Heuser, S. G. B., *Chem. Brit.*, 1977, **13**, 436

Interaction of ’iron blue’ pigment with ethylene oxide vapour at ambient temperature is highly exothermic and gives a product which ignites in contact with air [1]. The hazards of using undiluted ethylene oxide in sterilisers, and the need to use inert purging between vacuum degassing stages is stressed [2].

Lead chromate

See Lead chromate: Iron(III) hexacyanoferrate(4—)

See other METAL CYANIDES (AND CYANO COMPLEXES)

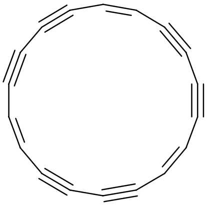
3733b. Tetrakis(butadiynyl)ethene (5,6-(Dibutadiynyl)-5-decen-1,3,7,9-tetrayne)
[ ] **$C_{18}H_4$**

$$\mathbf{(HC{\equiv}C\text{-}C{\equiv}C)_2C{=}C(C{\equiv}C\text{-}C{\equiv}C\text{-}H)_2}$$

See 1,10-Bis(trimethylsilyl)-5.6-bis(trimethylsilylbutadiynyl)dec-5-en-1,3,7,9-tetrayne

See other ALKYNES

3734. 1,7,13-Cyclooctadecatriene-3,5,9,11,15,17-hexayne (Hexahydro[18]annulene)
[16668-69-2] **$C_{18}H_6$**

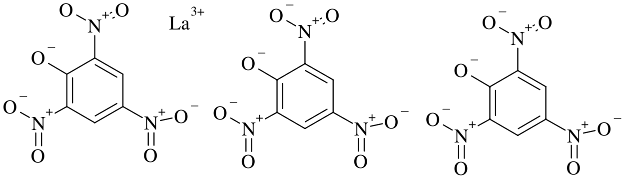


Diederich, F. *et al., Angew. Chem. (Int.)*, 1992, **31**(9), 1101

Explodes on heating to 85°C.

See other ALKYNES

3735. Lanthanum picrate
[16049-00-6] **$C_{18}H_6LaN_9O_{21}$**

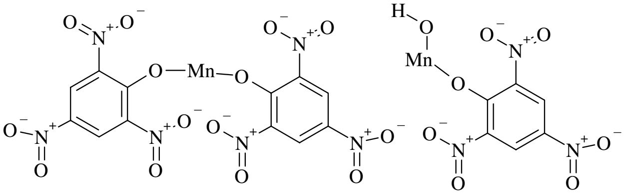


Tucholskii, T., *Rept. AD 633414*, Springfield (Va.), USNTIS, 1966

In a study of the thermal stability of the picrates of group III metals, that of lanthanum occasionally exploded prematurely on heating.

See other PICRATES

3736. Manganese picrate hydroxide
[41570-79-0] **$C_{18}H_7Mn_2N_9O_{22}$**



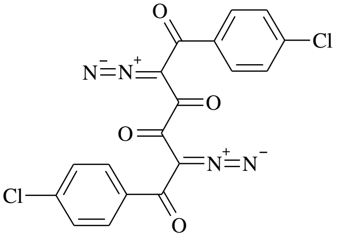
Bernardi, A., *Gazz. Chim. Ital.*, 1930, **60**, 169—171

The basic manganese picrate double salt,, and its 2,4-dinitro- and 2-nitro- analogues, all deflagrated violently on heating.

See other HEAVY METAL DERIVATIVES, METAL NITROPHENOXIDES, PICRATES, POLYNITROARYL COMPOUNDS

3737. 1,6-Bis(4-chlorophenyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane

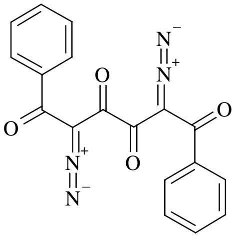
[76695-68-6] **$C_{18}H_8Cl_2N_4O_4$**



See 1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane (next below)
See other DIAZO COMPOUNDS

3738. 1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane

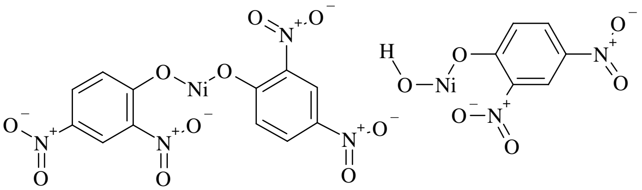
[76695-64-2] **$C_{18}H_{10}N_4O_4$**



Rubin. M. B. *et al., J. Chem. Soc., Perkin Trans. I*, 1980, 2671
The title compound and its 4,4'- chloro-, methyl- and methoxy-derivatives all decomposed violently at 155—165°C.
See other DIAZO COMPOUNDS

3739. Nickel 2,4-dinitrophenoxide hydroxide

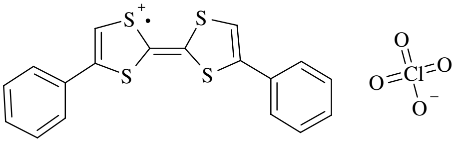
[ ] **$C_{18}H_{10}N_6Ni_2O_{16}$**



Bernardi, A., *Gazz. Chim. Ital.*, 1930, **60**, 166
It deflagrates very violently on heating.
See other HEAVY METAL DERIVATIVES, METAL NITROPHENOXIDES, POLYNITROARYL COMPOUNDS

3740. 4,4′-Diphenyl-2,2′-bi(1,3-dithiol)-2′-yl-2-ylium perchlorate

[53213-77-7] **$C_{18}H_{12}ClO_4S_4$**



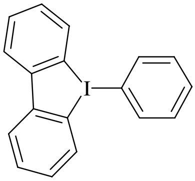
Sunderlin, K. G. R., *Chem. Eng. News*, 1974, **52**(31), 3

A few mg exploded violently during determination of the m.p., shattering the apparatus.

See other NON-METAL PERCHLORATES

3741. 9-Phenyl-9-iodafluorene (5-Phenyldibenzoiodole)

[32174-73-5] **$C_{18}H_{13}I$**



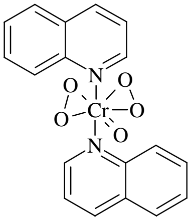
Banks, D. F., *Chem. Rev.*, 1966, **66**, 248

It explodes at 105°C.

See other IODINE COMPOUNDS

3742. Oxodiperoxodiquinolinechromium(VI)

[ ] **$C_{18}H_{14}CrN_2O_5$**

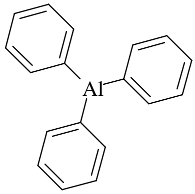


See Oxodiperoxodipyridinechromium(VI)

See other AMMINECHROMIUM PEROXOCOMPLEXES

3743. Triphenylaluminium

[841-76-9] **$C_{18}H_{15}Al$**



Water

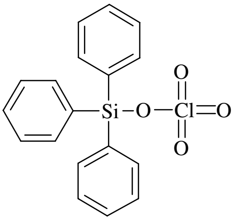
Neely, T. A. *et al., Org. Synth.*, 1965, **45**, 107

Triphenyl aluminium and its etherate evolved heat and sparks on contact with water.

See other ARYLMETALS

3744. Triphenylsilyl perchlorate

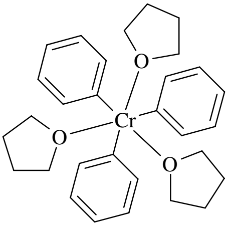
[101652-99-7] **$C_{18}H_{15}ClO_4Si$**



See entry ORGANOSILYL PERCHLORATES

3745. Triphenylchromium tetrahydrofuranate

[16462-53-6] **$C_{18}H_{15}Cr.3C_4H_8O$**



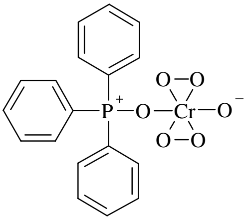
Diethyl ether

Bailar, 1973, Vol. 4, 974

On warming, or on treatment with ether, the solvated complex give a black pyrophoric material of unknown constitution.

See other ARYLMETALS

3746. Triphenylphosphine oxide-oxodiperoxochromium(VI)
[93228-65-0] **$C_{18}H_{15}CrO_6P$**

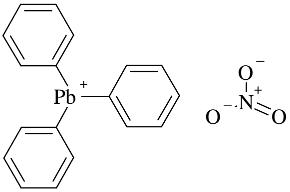


Daire, E. *et al., Nouv. J. Chim.*, 1984, **8**, 271—274

It effectively hydroxylates hydrocarbons but is free of the explosion risk of the analogous pyridine *N*-oxide complex.

See related AMMINECHROMIUM PEROXOCOMPLEXES

3747. Triphenyllead nitrate
[21483-08-9] (ion) **$C_{18}H_{15}NO_3Pb$**



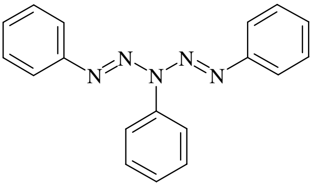
Sulfuric acid

Gilman, H. *et al., J. Org. Chem.*, 1951, **16**, 466

It ignites in contact with conc. acid

See related ARYLMETALS

3748. 1,3,5-Triphenyl-1,4-pentaazadiene
[30616-12-7] **$C_{18}H_{15}N_5$**



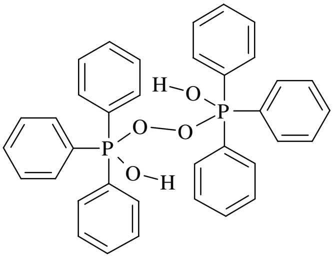
Sorbe, 1968, 141

It explodes at 80°C and is shock-sensitive.

See other HIGH-NITROGEN COMPOUNDS

3749. Triphenylphosphine oxide hydrogen peroxidate

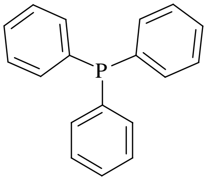
[3319-45-7] $C_{18}H_{15}OP.0.5H_2O_2$



Bradley, D. C. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 4
The 2:1 complex may explode.
See CRYSTALLINE HYDROGEN PEROXIDATES
See related REDOX COMPOUNDS

3750. Triphenylphosphine

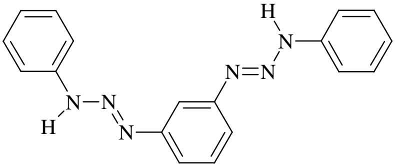
[603-35-0] $C_{18}H_{15}P$



Preparative hazard
See Sodium: Chlorobenzene, Phosphorus trichloride
See related ALKYLPHOSPHINES

3751. 1,3-Bis(phenyltriazeno)benzene

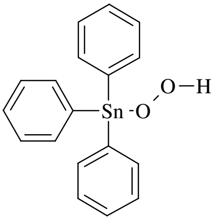
[70324-26-4] $C_{18}H_{16}N_6$



Kleinfeller, H., *J. Prakt. Chem. [2]*, 1928, **119**, 61
It explodes if heated rapidly.
See other TRIAZENES

3752. Triphenyltin hydroperoxide

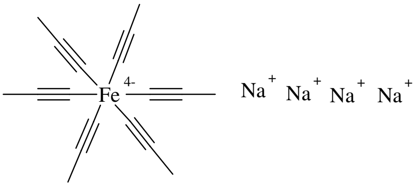
[4150-34-9] **$C_{18}H_{16}O_2Sn$**



Dannley, R. L. *et al., J. Org. Chem.*, 1965, **30**, 3845
It explodes reproducibly at 75°C.
See other ORGANOMETALLIC PEROXIDES

3753. Sodium hexakis(propynyl)ferrate(4—)

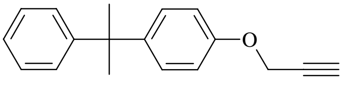
[ ] **$C_{18}H_{18}FeNa_4$**



Bailar, 1973, Vol. 3, 1025
An explosive complex salt.
See other COMPLEX ACETYLIDES

3754. 1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene

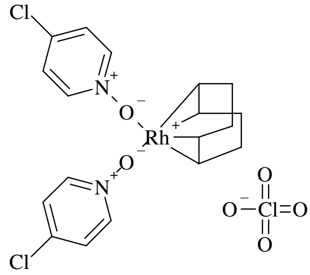
[ ] **$C_{18}H_{18}O$**



Douglas, W. E. *et al., J. Organomet. Chem.*, **444**(1—2), C62
Explosively polymerises when heated > 110°C in presence of nickelocene catalyst.
See VIOLENT POLYMERISATION
See other ACETYLENIC COMPOUNDS, POLYMERISATION INCIDENTS

3755. 1,5-Cyclooctadiene-bis(4-chloropyridine *N*-oxide)rhodium(I) perchlorate

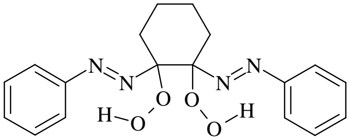
[80005-73-8] **$C_{18}H_{20}Cl_3N_2O_6Rh$**



Uson, R. *et al., J. Organomet. Chem.*, 1981, **217**, 252
The complex, one of a series of substituted pyridine derivatives, exploded violently during microanalytical combustion.
See related AMMINEMETAL OXOSALTS

3756. 1,2-Dihydroperoxy-1,2-bis(benzeneazo)cyclohexane

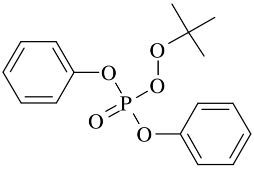
[71404-13-2] **$C_{18}H_{20}N_4O_4$**



See Oxygen: Cyclohexane-1,2-dione bis(phenylhydrazone)
See other α-PHENYLAZO HYDROPEROXIDES

3757. *O—O-tert*-Butyl di(4-tolyl) monoperoxophosphate

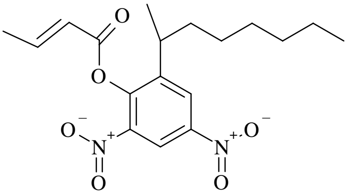
[ ] **$C_{18}H_{23}O_5P$**



Rieche, A. *et al., Chem. Ber.*, 1962, **95**, 385
The material deflagrated as a solid, or decomposed exothermally in its reaction mixture soon after preparation.
See other tert-BUTYL PEROXOPHOSPHATE DERIVATIVES, PHOSPHORUS ESTERS

3758. 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate

[27661-44-5] **$C_{18}H_{24}N_2O_6$**



Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 2

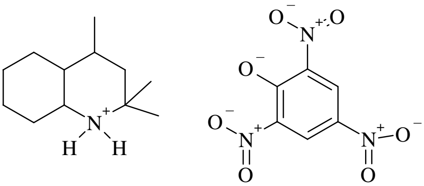
Decomposition and a pressure explosion occurred while a 10 kl tanker with steam-heating coils was being unloaded.

See other POLYNITROARYL COMPOUNDS

See related PEROXIDISABLE COMPOUNDS

3759. 2,2,4-Trimethyldecahydroquinolinium picrate

[ ] **$C_{18}H_{23}N_4O_7$**



2-(2-Butoxyethoxy)ethanol

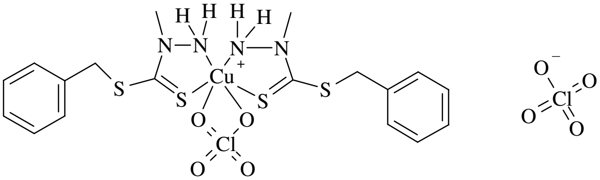
Franklin, N. C., private comm., 1967

Evaporation of a solution of the picrate in the diether (b.p. 230°C) caused a violent explosion. The solvent had probably peroxidised during open storage and the residual mixture of peroxide and picrate had exploded as evaporation proceeded. Use of peroxide-free solvent and lower (vacuum) evaporation temperature appeared to be safe.

See other PICRATES

3760. Bis(benzyl 1-methylhydrazinocarbodithioate N^2,S')(perchlorato-O,O')copper-(1+) perchlorate

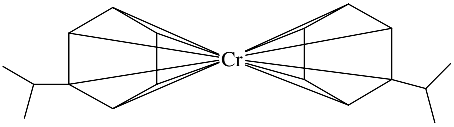
[67870-99-9] **$C_{18}H_{24}Cl_2CuN_4O_8S_4$**



See Bis-*O,N*[(*N*'-pent-2-en-2-oxy-4-ylidene)-*N,S*-dimethyldithiocarbazate]copper(II) perchlorate

3761a. Dicumenechromium(0)

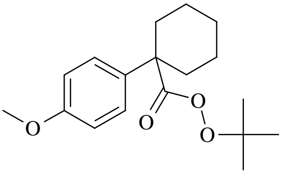
[12001-89-7] **$C_{18}H_{24}Cr$**



Aldrich catalogue, 1986
It is pyrophoric.
See other ARYLMETALS, ORGANOMETALLICS

3761b. 1,1-Dimethylethyl 1-(4-methoxyphenyl)cyclohexanepercarboxylate

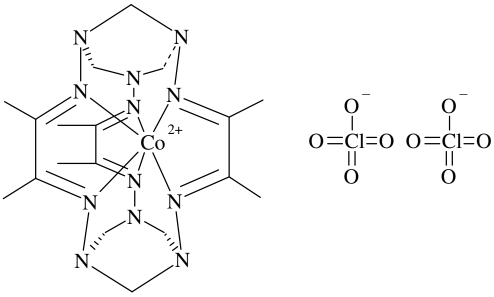
[ ] **$C_{18}H_{26}O_4$**



Wolf, R. A. *et al., J. Org. Chem.*, 1998, **63**(12), 3814
A neat sample of this material, prepared as part of a study of thermal decomposition of arylcycloalkanepercarboxylates, spontaneously exothermed to explosion. One would expect it to have been one of the more stable of those studied. It is recommended that neat samples of such compounds be kept cold and handled with caution and protective equipment.
See other PEROXYESTERS

3762. 5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo[8.8.4.$1^{3,17}$.$1^{8,12}$]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22}cobalt(II) perchlorate

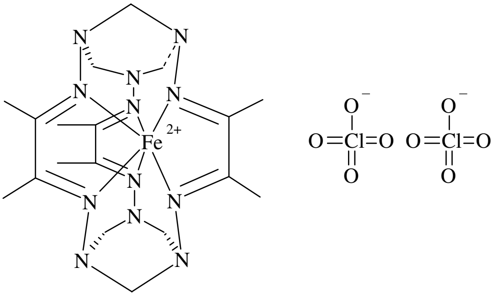
[72644-04-3] **$C_{18}H_{30}Cl_2CoN_{12}O_8$**



See entry CLATHROCHELATED METAL PERCHLORATES

3763. 5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo[8.8.4.1^{3,17}.1^{8,12}]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22}iron(II) perchlorate

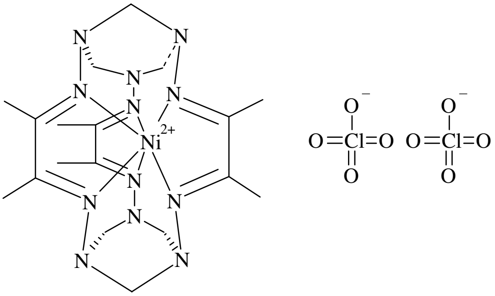
[75516-37-9] **$C_{18}H_{30}Cl_2FeN_{12}O_8$**



See entry CLATHROCHELATED METAL PERCHLORATES

3764. 5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo[8.8.4.1^{3,17}.1^{8,12}]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22}nickel(II) perchlorate

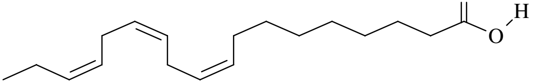
[63128-08-5] **$C_{18}H_{30}Cl_2N_{12}NiO_8$**



See entry CLATHROCHELATED METAL PERCHLORATES

3765. 9,12,15-Octadecatrienoic acid (Linolenic acid)

[463-40-1] **$C_{18}H_{30}O_2$**



Cobalt naphthenate

Kotoyori, T., *Chem. Abs.*, 1980, **93**, 221950

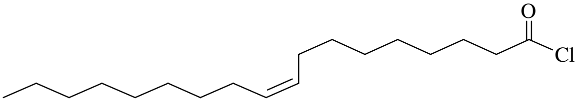
Model experiments on the mixture (simulating paint tailings) exposed to air showed that storage at low temperature (7°C) led to a larger build-up of peroxide than occurred at 35°C. This would account for spontaneous ignition of paint tailings (residues) stored at low temperature and subsequently heated to 60°C.

See AUTOXIDATION

See other ORGANIC ACIDS

3766. Oleoyl chloride (*cis*-9-Octadecenoyl chloride)

[112-77-6] **$C_{18}H_{33}ClO$**



'Acid tars'

Anon., *Jahresbericht*, 1994, 74

The residue of a sample of 'olein chloride' (crude oleoyl chloride) was tipped into a waste container containing 'acid tars' (70—80% waste sulfuric acid). There was a vigorous reaction, with gas evolution, which sprayed the analytical technician involved with the liquid contents of the container, causing burns.

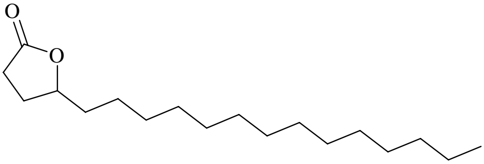
Nitric acid

See Nitric acid: Oleoyl chloride

See other ACYL HALIDES

3767. 1,4-Octadecanolactone

[502-26-1] **$C_{18}H_{34}O_2$**

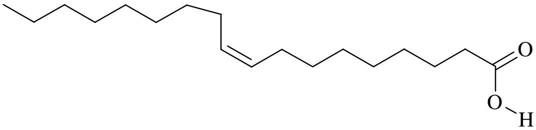


Preparative hazard

See Perchloric acid: Oleic acid

3768. *cis*-9-Octadecenoic acid (Oleic acid)

[112-80-1] **$C_{18}H_{34}O_2$**



HCS 1980, 701

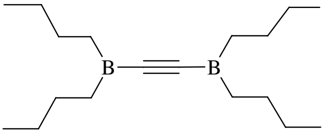
Aluminium

See Aluminium: Oleic acid

Perchloric acid
See Perchloric acid: Oleic acid
See other ORGANIC ACIDS

3769. Bis(dibutylborino)acetylene

[ ] $C_{18}H_{36}B_2$



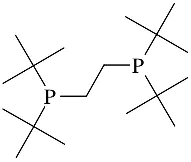
Hartmann, H. *et al., Z. Anorg. Chem.*, 1959, **299**, 174

Both the n- and iso-derivatives ignite in air.

See other ACETYLENIC COMPOUNDS, ALKYLBORANES

3770. 1,2-Bis(di-*tert*-butylphosphino)ethane

[107783-62-0] $C_{18}H_{40}P_2$



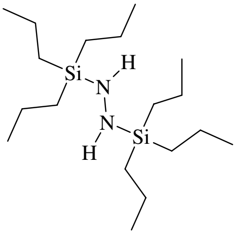
Benn, R. *et al., Z. Naturforsch. B*, 1986, **41B**, 680—691

The ligand, like its lower homologues, is pyrophoric in air.

See related ALKYLPHOSPHINES

3771. 1,2-Bis(tripropylsilyl)hydrazine

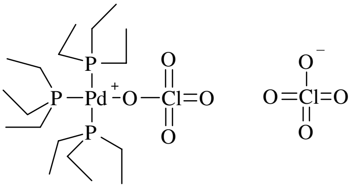
[13271-98-2] $C_{18}H_{44}N_2Si_2$



See entry SILYLHYDRAZINES
See related ALKYLSILANES

3772. Perchloratotris(triethylphosphine)palladium(II) perchlorate

[94288-47-8] **$C_{18}H_{45}Cl_2O_8P_3Pd$**



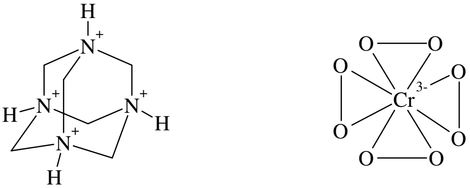
Bruce, D. W. *et al., J. Chem. Soc., Dalton Trans.*, 1984, 2252

It explodes on heating.

See related AMMINEMETAL OXOSALTS, METAL PERCHLORATES, PLATINUM COMPOUNDS

3773. Hexamethylenetetrammonium tetraperoxochromate(V)?

[ ] **$C_{18}H_{48}Cr_4N_{12}O_{32}$**



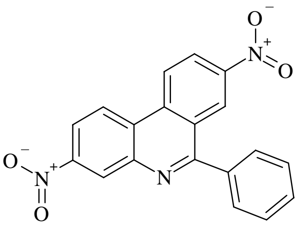
House, D. A. *et al., Inorg. Chem.*, 1966, **6**, 1078, footnote 8

Material (believed to be the title compound) recrystallised from water, and washed with methanol to dry by suction, ignited and then exploded on the filter funnel.

See related AMMINECHROMIUM PEROXOCOMPLEXES, AMMINEMETAL OXOSALTS

3774. 3,8-Dinitro-6-phenylphenanthridine

[82921-86-6] **$C_{19}H_{11}N_3O_4$**



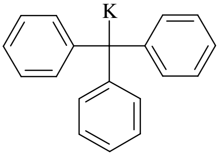
Diethyl sulfate

See Diethyl sulfate: 3,8-Dinitro-6-phenylphenanthridine

See other POLYNITROARYL COMPOUNDS

3775. Triphenylmethylpotassium

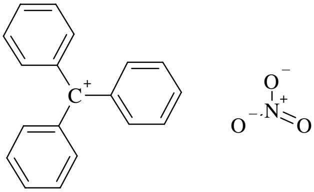
[1528-27-4] **$C_{19}H_{15}K$**



Houben-Weyl, 1970, Vol. 13.1, 269
The dry powder ignites in air.
See other ORGANOMETALLICS

3776. Triphenylmethyl nitrate

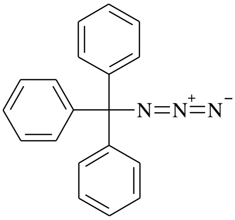
[111422-41-4] **$C_{19}H_{15}NO_3$**



Lewis acids
See entry ALKYL NITRATES

3777. Triphenylmethyl azide

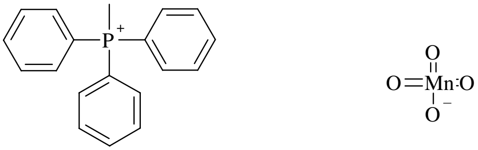
[14309-25-2] **$C_{19}H_{15}N_3$**



Robillard, J. J., Ger. Offen. 2 345 787, 1974
The unstable explosive azide may be stabilised by adsorption for reprographic purposes.
See other ORGANIC AZIDES

3778. Methyltriphenylphosphonium permanganate

[73335-41-8] **$C_{19}H_{18}MnO_4P$**



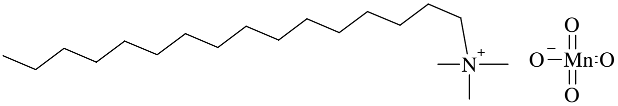
1. Reischl, W. *et al., Tetrahedron*, 1979, **35**, 1109—1110
2. Leddy, B. P. *et al., Tetrahedron Lett.*, 1980, **21**, 2261—2262

It decomposes explosively above 70° [1], or at 80—90°C [2].

See other QUATERNARY OXIDANTS

3779. Hexadecyltrimethylammonium permanganate (Cetyltrimethylammonium permanganate)

[73257-07-5] **$C_{19}H_{42}MnNO_4$**



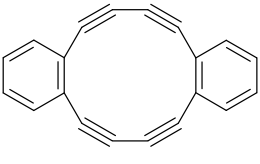
Dash, S. *et al., Chem. Abs., 1995,* **123**, 227457m

Stable when kept in the dark at room temperature, it decomposes violently at 115°C.

See other QUATERNARY OXIDANTS

3780. Dibenzocyclododeca-1,7-dienetetrayne (5,6,7,8,13,14,15,16-Octadehydrodibenzo[*a,g*]cyclododecene)

[7203-21-6] **$C_{20}H_8$**

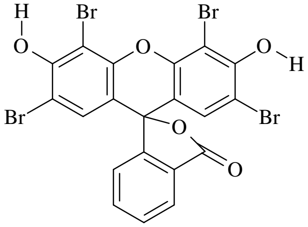


Guo, L. *et al., J. Chem. Soc., Chem. Comm.*, 1994, (3), 243

An unstable synthetic byproduct, attributed the above structure, explodes when scratched in air, leaving carbon as the residue. It blackens rapidly even in vacuum.

See other ACETYLENIC COMPOUNDS

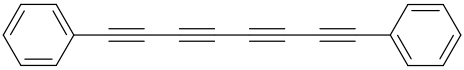
3781. 2′,4′,5′,7′-Tetrabromo-3′,6′-dihydroxyspiro[isobenzofuran-1(3*H*),9′-[9*H*]xanthen-3-one (Eosin)
[15876-39-8] [122530-01-2] **$C_{20}H_8Br_4O_5$**



Lead salts, Red lead

See Dilead(II)lead(IV) oxide: Eosin

3782. 1,8-Diphenyloctatetrayne
[4572-12-7] **$C_{20}H_{10}$**

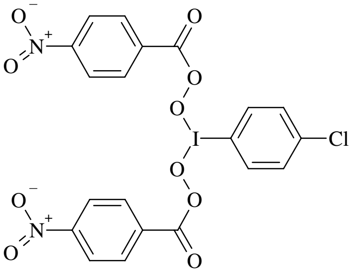


Nakagawa, M., *Chem. Abs.*, 1951, **45**, 7082a

Though stable in the dark at ambient temperature for a year, when exposed to light on a metal plate it decomposed explosively.

See other ALKYNES, IRRADIATION DECOMPOSITION INCIDENTS

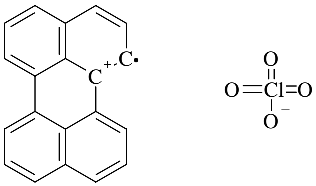
3783. *I,I*-Bis(4-nitrobenzoylperoxy)-4-chlorophenyliodine
[56391-49-2] **$C_{20}H_{12}ClIN_2O_{10}$**



See entry I,I-DI(BENZOYLPEROXY)ARYLIODINES

3784. Perylenium perchlorate

[12576-63-5] **$C_{20}H_{12}Cl_2O_8$**



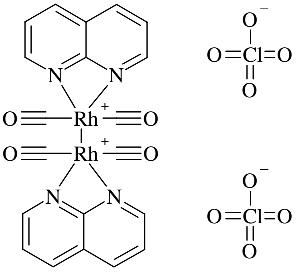
Rosseinsky, D. R. *et al., J. Chem. Soc., Perkin Trans. 2*, 1985, 135—138

The title compound, prepared by electrolysis of perylene and tetrabutylammonium perchlorate in nitrobenzene, exploded on contact with nickel. Co-produced compounds should also be handled with caution and in small amounts, especially in contact with metals.

See other NON-METAL PERCHLORATES

3785. Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate

[90635-49-7] **$C_{20}H_{12}Cl_2N_4O_{12}Rh_2$**



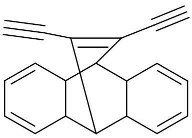
Camellini, A. T. *et al., J. Chem. Soc., Dalton Trans.*, 1984, 130

Attempted microanalytical combustion of old samples of the salt or its 2-methyl homologue led to violent explosions.

See related AMMINEMETAL OXOSALTS, CARBONYLMETALS

3786. 11,12-Diethynyl-9,10-dihydro-9,10-ethenoanthracene

[126487-13-6] **$C_{20}H_{12}$**



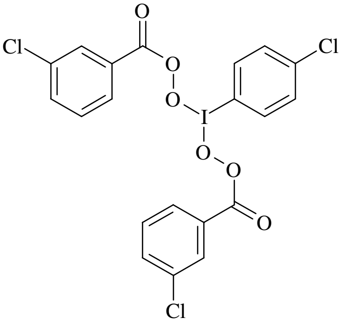
Diederich, F. *et al., Angew. Chem. (Int.)*, 1992, **31**(9), 1101

The crystalline solid has been known to explode spontaneously.

See other ALKYNES

3787. *I,I*-Bis(3-chlorobenzoylperoxy)-4-chlorophenyliodine

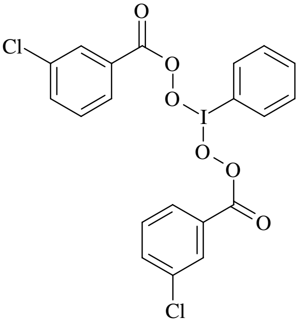
[ ] **$C_{20}H_{12}Cl_3IO_6$**



See entry I,I-DI(BENZOYLPEROXY)ARYLIODINES

3788. *I,I*-Bis(3-chlorobenzoylperoxy)phenyliodine

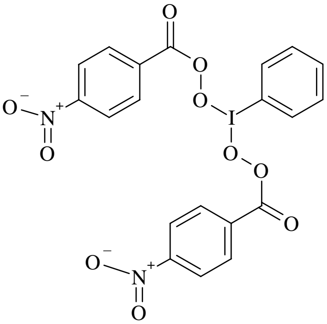
[30242-75-2] **$C_{20}H_{13}Cl_2IO_6$**



See entry I,I-DI(BENZOYLPEROXY)ARYLIODINES

3789. *I,I*-Bis(4-nitrobenzoylperoxy)phenyliodine

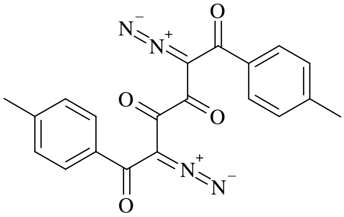
[30030-30-9] **$C_{20}H_{13}IN_2O_{10}$**



See entry I,I-DI(BENZOYLPEROXY)ARYLIODINES

3790. 1,6-Di(4’-tolyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane

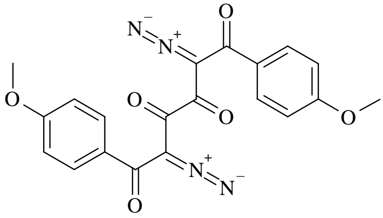
[76695-67-5] **$C_{20}H_{14}N_4O_4$**



See 1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane

3791. 1,6-Di(4’-methoxyphenyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane

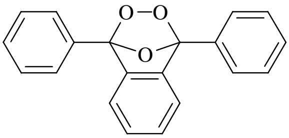
[76695-66-4] **$C_{20}H_{14}N_4O_6$**



See 1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane

3792. 2,5-Diphenyl-3,4-benzofuran-2,5-endoperoxide (1,4-Epoxy-1,4-dihydro-1,4-diphenyl-2,3-benzodioxin)

[41337-62-6] **$C_{20}H_{14}O_3$**



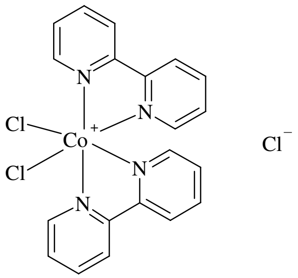
Alone, or Carbon disulfide

1. Dufraisse, C. *et al., Compt. rend.*, 1946, **223**, 735
2. Rio, G. *et al., J. Chem. Soc., Chem. Comm.*, 1982, 72

Formally an ozonide, this photo-peroxide explodes at 18°C [1], and its dimerisation, catalysed by carbon disulfide, was exothermic and sometimes explosive at ambient temperature [2].

See other CYCLIC PEROXIDES, OZONIDES

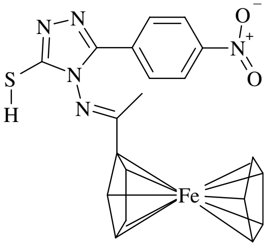
3793a. *cis*-Dichlorobis(2,2'-bipyridyl)cobalt(III) chloride
[23380-38-3 or 14522-39-5] **$C_{20}H_{16}Cl_3CoN_4$**



Preparative hazard

See Chlorine: Cobalt(II) chloride, Methanol

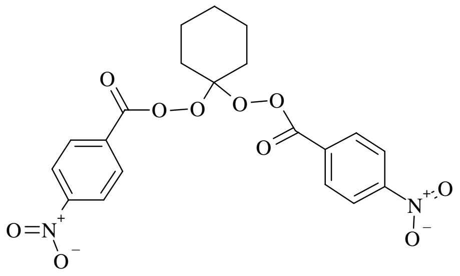
3793b. 1-[[3-(4-Nitrophenyl)-5-thiolato-1,2,4-triazol-4-yl]imino]ethylferrocene (1-[[3-(4-Nitrophenyl)-5-mercapto-1,2,4-triazol-4-yl]imino]ethylferrocene) (1-[[1,5-Dihydro-3-(4-nitrophenyl)-5-thioxo-*4*H-1,2,4-triazol-4-yl]imino]ethyl]ferrocene)
[271247-92-8] **$C_{20}H_{17}FeN_5O_2S$**



Sengupta, S. K. *et al., Transition Met. Chem.*, 2000, **25**(2), 150

Three to one lanthanum and praseodymium salts were prepared. They exploded on heating above 180 C, making thermal studies difficult. Analogues without the nitro-group decompose controllably.

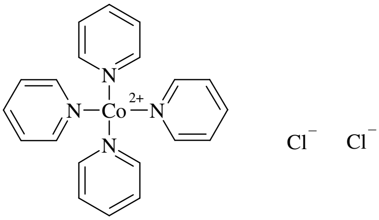
3794. 1,1-Bis(4-nitrobenzoylperoxy)cyclohexane
[ ] **$C_{20}H_{18}N_2O_{10}$**



Criegee, R. *et al., Ann.*, 1948, **560**, 135
It explodes at 120°C.
See other PEROXYESTERS

3795. Tetrapyridinecobalt(II) chloride

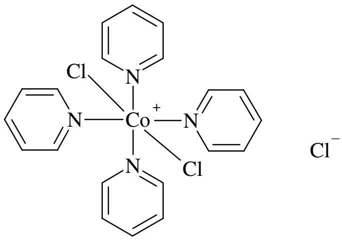
[13985-87-0] **$C_{20}H_{20}Cl_2CoN_4$**



Chlorine, Methanol
See Chlorine: Methanol, Tetrapyridinecobalt(II) chloride

3796. *trans*-Dichlorotetrapyridinecobalt(III) chloride (Dichlorotetrakispyridinecobalt(1+) chloride)

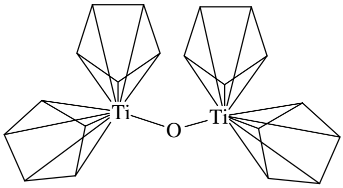
[14077-02-2 or 27883-34-7] **$C_{20}H_{20}Cl_3CoN_4$**



Preparative hazard
See Chlorine: Methanol, Tetrapyridinecobalt(II) chloride

3797. Oxybis[bis(cyclopentadienyl)titanium]

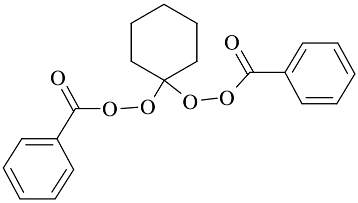
[51269-39-7] **$C_{20}H_{20}OTi_2$**



Bottomley, F. *et al., J. Amer. Chem. Soc.*, 1980, **102**, 5241
The dry solid is explosively oxidised in contact with air.
See other ORGANOMETALLICS

3798. 1,1-Bis(benzoylperoxy)cyclohexane

[13213-29-1] **$C_{20}H_{20}O_6$**



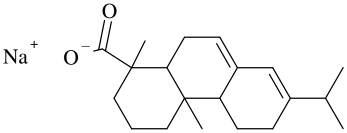
Criegee, R. *et al., Ann.*, 1948, **560**, 135

It explodes sharply in a flame.

See other PEROXYESTERS

3799. Sodium abietate

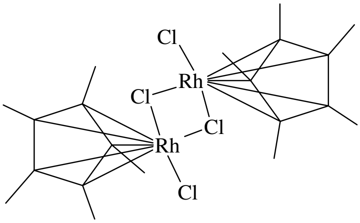
[14351-66-7] **$C_{20}H_{29}NaO_2$**



See entry METAL ABIETATES

3800. Dichlorodi-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium

[12354-85-7] **$C_{20}H_{30}Cl_4Rh_2$**



Air, Alkylmetals

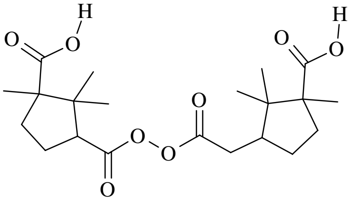
Isobe, K. *et al., J. Chem. Soc., Dalton Trans.*, 1983, 1445

In preparation of di-μ-methylenebis(methyl-pentamethylcyclopentadienyl)dirhodium complexes by aerobic oxidation of a solution of the halocomplex and methyllithium or trimethylaluminium in ether—benzene, the reaction mixture occasionally ignited and burned violently. Full precautions and a working scale below 1 mmol are recommended.

See related ALKYLMETAL HALIDES

3801. Di-3-camphoroyl peroxide

[ ] **$C_{20}H_{30}O_8$**



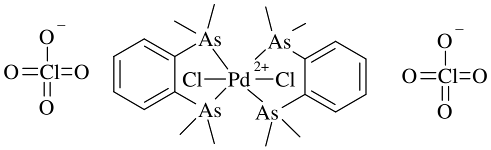
Milas, N. A. *et al., J. Amer. Chem. Soc.*, 1933, **55**, 350—351

Explosive decomposition occurred at the m.p., 142°C, or on exposure to flame.

See other DIACYL PEROXIDES

3802. *trans*-Dichlorobis[1,2-phenylenebis(dimethylarsine)]palladium(IV) diperchlorate

[60489-76-1] **$C_{20}H_{32}As_4Cl_4O_8Pd$**



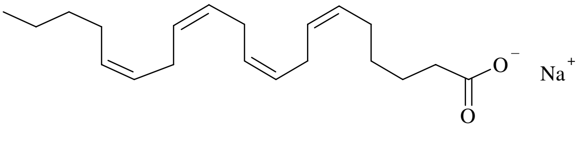
Gray, L. R. *et al., J. Chem. Soc., Dalton Trans.*, 1983, 33—41

Though no explosions occurred during the preparation by addition of 75% perchloric acid to solutions of the complex in conc. nitric/hydrochloric acid mixtures, this and the amino- and phosphino-analogues are potentially unstable.

See related AMMINEMETAL OXOSALTS

3803. Sodium 5,8,11,14-eicosatetraenoate (Sodium arachidonate)

[6610-25-9] **$C_{20}H_{32}NaO_2$**



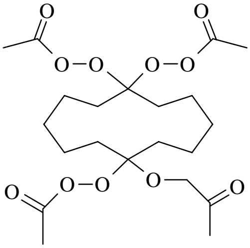
Henderson, J. D. *et al., Chem. Eng. News*, 1983, **61**(33), 2

An opened 100 mg ampoule of the salt was stored dark in a desiccator at —20°C between occasional samplings during a few months. A few minutes after return to storage, the ampoule contents decomposed violently. It was supposed that peroxide formation (and perhaps polymerisation of the polyene) was involved in the incident.

See other PEROXIDISABLE COMPOUNDS

3804. 1,1,6,6-Tetrakis(acetylperoxy)cyclododecane

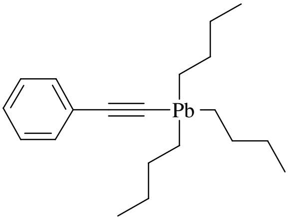
[ ] **$C_{20}H_{32}O_{12}$**



Criegee, R. *et al., Ann.*, 1948, **560**, 135
Weak friction causes strong explosion.
See other PEROXYESTERS

3805. Tributyl(phenylethynyl)lead (Tris(Dimethylethyl)(phenylethynyl)plumbane)

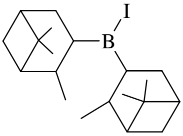
[21249-40-1] **$C_{20}H_{32}Pb$**



Houben-Weyl., 1975, Vol. 13.3, 80
Violent decomposition occurred during attempted distillation.
See related ALKYLMETALS, METAL ACETYLIDES

3806. *B*-Iododiisopinocampheylborane (Iodobis(2,6,6-trimethylbicyclo[3.1.1]hept-3-yl)borane)

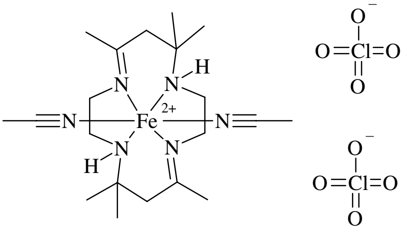
[116005-09-5] **$C_{20}H_{34}BI$**



Brown, H. C. *et al., Heteroat. Chem.*, 1995, **6**(2), 117
Pyrophoric, very hygroscopic, fumes in air.
See other ALKYLHALOBORANES

3807. Diacetonitrile-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate

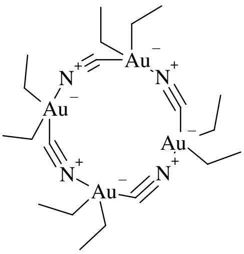
[50327-56-5] **$C_{20}H_{38}Cl_2FeN_6O_8$**



See entry [14] DIENE-N_4 COMPLEXES

3808a. Tetracyanooctaethyltetragold

[ ] **$C_{20}H_{40}Au_4N_4$**



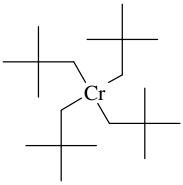
Burawoy, A. *et al., J. Chem. Soc.*, 1935, 1026

This tetramer of cyanodiethylgold is friction-sensitive and also decomposes explosively above 80°C. The propyl homologue is not friction-sensitive, but also decomposes explosively on heating in bulk.

See other CYANO COMPOUNDS, GOLD COMPOUNDS

3808b. Tetrakis(2,2-dimethylpropyl)chromium

[37007-84-4] **$C_{20}H_{44}Cr$**



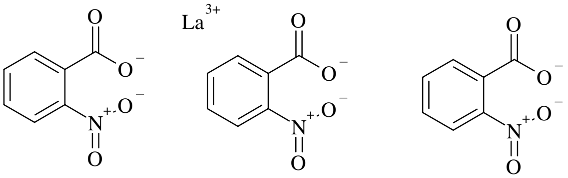
Schulzke, C. *et al., Organometallics*, 2002, **21**(18), 3810

It is pyrophoric, as is the analogue in which the quaternary carbons are replaced by silicon.

See other ALKYLMETALS

3809. Lanthanum 2-nitrobenzoate

[114515-72-9] **$C_{21}H_{12}LaN_3O_{12}$**



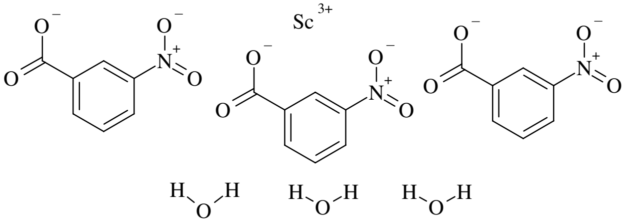
Ferenc, W. *et al., Monatsh. Chem.*, 1987, **118**, 1087—1100

Preparation of the 2-nitrobenzoate salts of yttrium and the lanthanide metals (except praseodymium) as mono- or di-hydrates was studied. All melted and decomposed explosively above 250°C.

See other HEAVY METAL DERIVATIVES, NITROARYL COMPOUNDS

3810. Scandium 3-nitrobenzoate

[111016-97-8] **$C_{21}H_{12}N_3O_{12}Sc$**



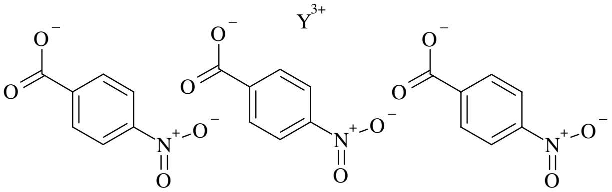
Brzyska, W. *et al., J. Therm. Anal.*, 1987, **32**, 671—678

After loss of the hemi-hydrate water, the anhydrous complex decomposes explosively on further heating.

See other HEAVY METAL DERIVATIVES, NITROARYL COMPOUNDS

3811. Yttrium 4-nitrobenzoate trihydrate

[115627-20-8] **$C_{21}H_{12}N_3O_{12}Y.3H_2O$**

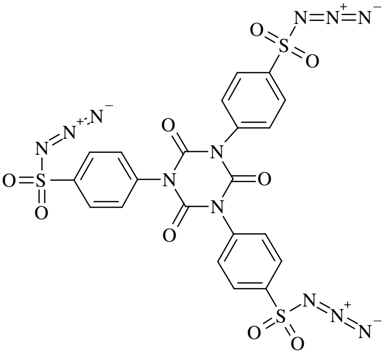


Ferenc, W. *et al., Monatsh. Chem.*, 1988, **119**, 407—424

The yttrium, lanthanum and other lanthanide salts exploded after dehydration during heating to above 300°C.

See other HEAVY METAL DERIVATIVES, NITROARYL COMPOUNDS

3812. 1,3,5-Tris(4-azidosulfonylphenyl)-1,3,5-triazinetrione
[31328-33-3] **$C_{21}H_{12}N_{12}O_9S_3$**

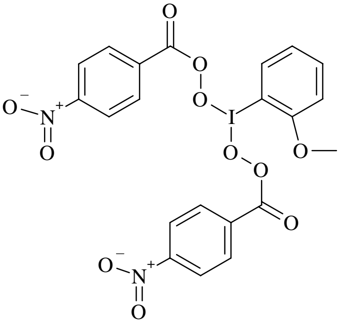


Ulrich, H. *et al., J. Org. Chem.*, 1975, **40**, 804

This trimer of 4-azidosulfonylphenylisocyanate melts at 200°C with violent decomposition.

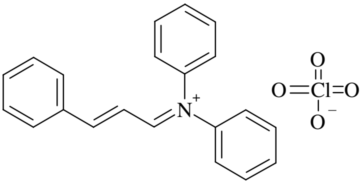
See other ACYL AZIDES

3813. *I,I*-Bis(4-nitrobenzoylperoxy)-2-methoxyphenyliodine
[ ] **$C_{21}H_{15}IN_2O_{11}$**



See entry *I,I*-DI(BENZOYLPEROXY)ARYLIODINES

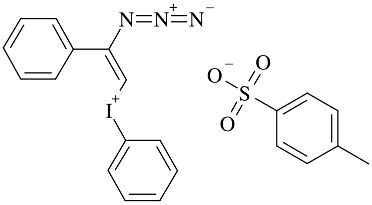
3814. *N,N*-Diphenyl-3-phenylpropenylidenimmonium perchlorate
[77664-36-9] **$C_{21}H_{18}ClNO_4$**



Qureshi, M. *et al., J. Indian Chem. Soc.*, 1980, **57**, 915—917

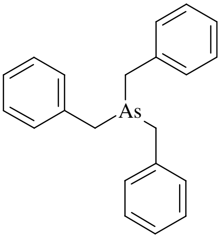
The immonium salt explodes on heating.
See other PERCHLORATE SALTS OF NITROGENOUS BASES

3815. *I*-(2-Azido-2-phenylvinyl)phenyliodonium 4-toluenesulfonate
[118235-47-5] **$C_{21}H_{18}IN_3O_3S$**



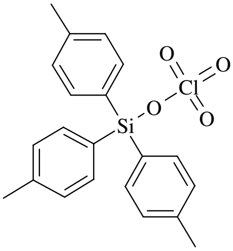
Kitamura, T. *et al., Tetrahedron Lett.*, 1988, **29**, 1887—1890
It decomposes explosively on melting.
See other IODINE COMPOUNDS, ORGANIC AZIDES

3816. Tribenzylarsine
[5888-61-9] **$C_{21}H_{21}As$**



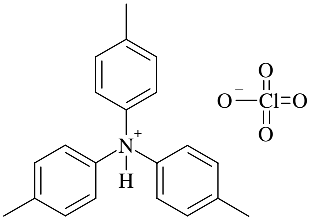
Dondorov, J. *et al., Ber.*, 1935, **68**, 1255
The pure material oxidises slowly at first in air at ambient temperature, but reaction becomes violent through autocatalysis.
See other ALKYLNON-METALS, BENZYL COMPOUNDS

3817. Tri-4-methylphenylsilyl perchlorate
[ ] **$C_{21}H_{21}ClO_4Si$**



See entry ORGANOSILYL PERCHLORATES

3818. Tri(4-tolyl)ammonium perchlorate [34729-49-2] $C_{21}H_{22}ClNO_4$

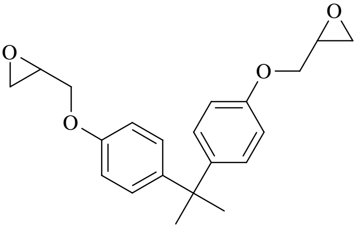


Weitz, E. *et al., Ber.*, 1926, **59**, 2307

It explodes violently when heated above the m.p., 123°C.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

3819. 2,2-Bis[4(2′,3′-epoxypropoxy)phenyl]propane [1675-54-3] $C_{21}H_{24}O_4$

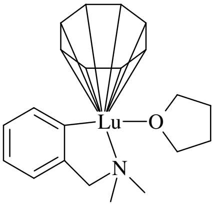


Trichloroethylene

See Trichloroethylene: Epoxides

See other 1,2-EPOXIDES

3820. (η^8 1,3,5,7-Cyclooctatetraene)[2-(dimethylaminomethyl)phenyl-*C,N*](tetrahydrofuran)lutetium [84582-81-0] $C_{21}H_{28}LuNO$

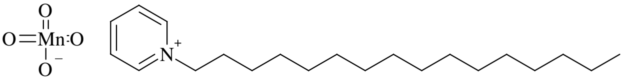


Wayda, A. L., *Inorg. Synth.*, 1990, **27**, 150

The dry powder may ignite spontaneously in air, partially oxidised samples can explode.

See related ORGANOMETALLICS

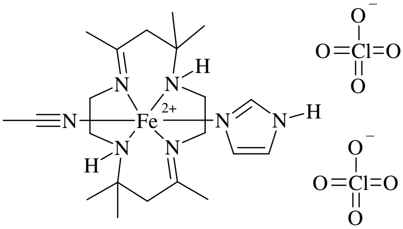
3821. *N*-Hexadecylpyridinium permanganate
[76710-77-5] **$C_{21}H_{38}MnNO_4$**



It explodes at 80—90°C.

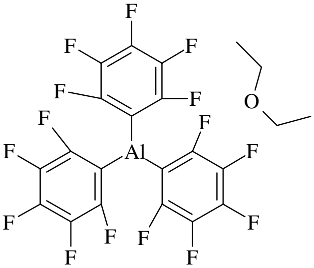
See entry QUATERNARY OXIDANTS

3822. Acetonitrileimidazole-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate
[36691-99-3] **$C_{21}H_{39}Cl_2FeN_7O_8$**



See entry [14] DIENE-N_4 COMPLEXES

3823. [1,1′-Oxybis[ethane]]tris(pentafluorophenyl)aluminium (Tris(pentafluorophenyl)aluminium etherate)
[14524-44-8] **$C_{22}H_{10}AlF_{15}O$**

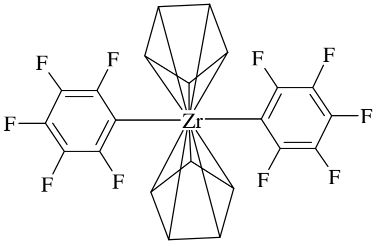


Pohlmann, J. L. W. *et al., Z. Naturforsch.*, 1965, **20b**(1), 5

This compound sometimes explodes on heating.

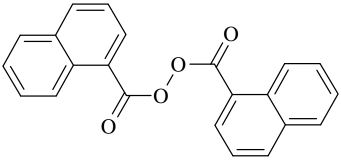
See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

3824. Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium
[12097-97-1] $C_{22}H_{10}F_{10}Zr$



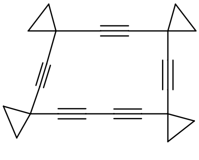
Chaudhari, M. A. *et al., J. Chem. Soc. (A)*, 1966, 838
It explodes in air (but not nitrogen) above the m.p., 219°C.
See other HALO-ARYLMETALS, ORGANOMETALLICS

3825. Di-1-naphthoyl peroxide
[29903-04-6] $C_{22}H_{14}O_4$



Castrantas, 1965, 17
It explodes on friction.
See other DIACYL PEROXIDES

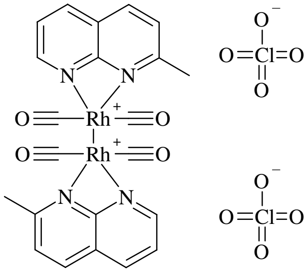
3826. Tetraspiro[2.2.2.2.2.2.4]docosa-4,9,14,19,21pentyne
[159148-53-5] $C_{22}H_{16}$



Scott, L. T. *et al., J. Amer. Chem. Soc.*, 1994, **116**(22), 10275
This compound melted at 155°C with decomposition, one sample exploded in an oil bath at 192°C.
See also ROTANES
See other ALKYNES

3827. Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate

[90635-53-3] **$C_{22}H_{16}Cl_2N_4O_{12}Rh_2$**

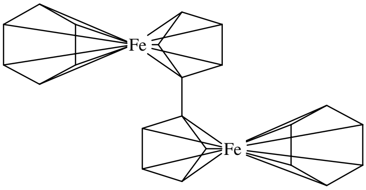


See Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate

See related AMMINEMETAL OXOSALTS, CARBONYLMETALS

3828. Bis(benzeneiron)—fulvalenediyl complex

[78398-48-8] **$C_{22}H_{20}Fe_2$**



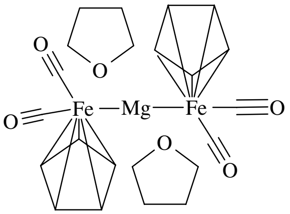
Desbois, M. H. *et al., J. Amer. Chem. Soc.*, 1985, **107**, 5280—5282

Unstable above —10°C, it burns explosively on contact with air.

See other ORGANOMETALLICS

3829. Bis(dicarbonylcyclopentadienyliron)—bis(tetrahydrofuran)magnesium

[55800-08-3] **$C_{22}H_{26}Fe_2MgO_6$**



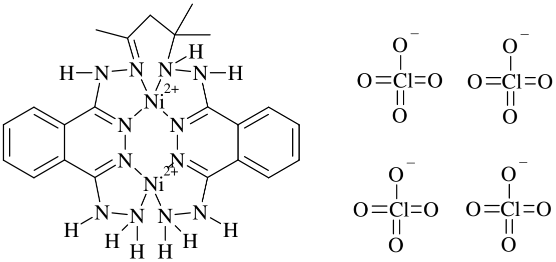
McVicker, G. B., *Inorg. Synth.*, 1976, **16**, 56—58

This, like other transition metal carbonyl derivatives of magnesium, is pyrophoric.

See other CARBONYLMETALS, ORGANOMETALLICS

3830. 4-[2-(4-Hydrazino-1-phthalazinyl)hydrazino]-4-methyl-2-pentanone(4-hydrazino-1-phthalazinyl)hydrazonedinickel(II) tetraperchlorate

[9018-45-5] $C_{22}H_{28}N_{12}Ni_2Cl_4O_{16}$



Rosen, W., *Inorg. Chem.*, 1971, **10**, 1833

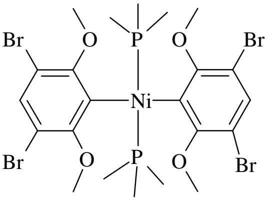
The green polymeric complex isolated directly from the reaction mixture explodes fairly violently at elevated temperatures. The tetrahydrate produced by recrystallisation from aqueous methanol is also moderately explosive when heated rapidly.

See other AMMINEMETAL OXOSALTS

See related TETRAAZAMACROCYCLANEMETAL PERCHLORATES

3831. Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel

[83459-96-5] $C_{22}H_{32}Br_4NiO_4P_2$



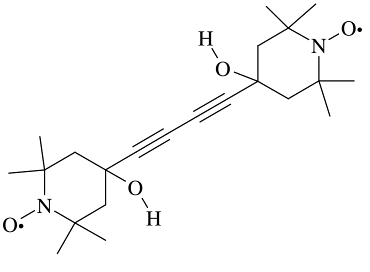
Wada, S. *et al., J. Chem. Soc., Dalton Trans.*, 1982, 1446

The complex decomposed explosively at 194°C.

See related ALKYLPHOSPHINES, HALO-ARYLMETALS

3832. 4,4′-(Butadiyne-1,4-diyl)bis(2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl)

[14306-88-8] $C_{22}H_{34}N_2O_4$



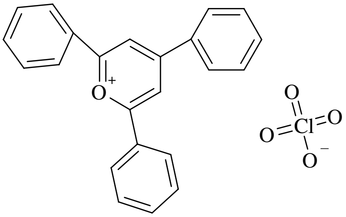
Miller, J. S. *et al., Chem. Mater.*, 1990, **2**(1), 60

Both crystalline forms decompose explosively to lower molecular weight products at 140°C under nitrogen.

See related ALKYNES

3833. 2,4,6-Triphenylpyrilium perchlorate

[1484-88-4] **$C_{23}H_{17}ClO_5$**



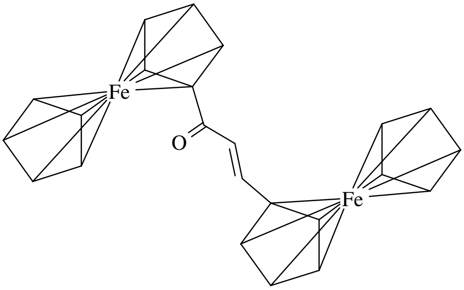
Pelter, A., *Chem. Abs.*, 1981, **95**, 97643 (reference to *Tetrahedron Lett.* original is incorrect)

Though not as sensitive as 1,3-benzodithiolium perchlorate, this salt is also explosive.

See other NON-METAL PERCHLORATES

3834. 1,3-Di[bis(cyclopentadienyl)iron]-2-propen-1-one

[12171-97-0] **$C_{23}H_{20}Fe_2O$**



Perchloric acid, Acetic anhydride, Cyclopentanone, Ether, Methanol

Anon., *Chem. Eng. News*, 1966, **44**(49), 50

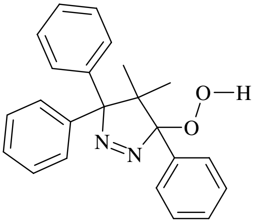
Condensation of the iron complex with cyclopentanone in perchloric acid—acetic anhydride—ether medium had been attempted. The non-crystalline residue, after methanol washing and drying in air for several weeks, exploded on being disturbed. This was attributed to possible presence of a derivative of ferrocenium perchlorate, a powerful explosive and detonator. However, methyl or ethyl perchlorates alternatively may have been involved.

See Perchloric acid: Acetic anhydride, etc., or: Diethyl ether

See other ORGANOMETALLICS

3835. 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3*H*)pyrazole (4,5-Dihydro-4,4-dimethyl-3,5,5-triphenyl-3*H*-pyrazol-3-yl hydroperoxide)

[133610-01-2] **$C_{23}H_{22}N_2O_2$**



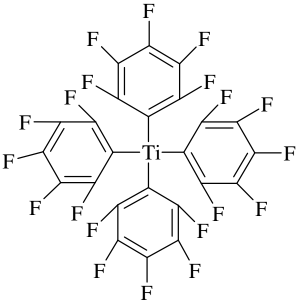
Baumstark, A. L, *et al., J. Heterocyclic Chem.*, 1991, **28**(1), 113

This, the most stable of 5 homologues, the others having one or two aryl substituents replaced by methyl, exploded at 90°C in a melting point determination. It appears that azohydroperoxy compounds are even more explosive than the sum of their parts might indicate.

See related ORGANIC PEROXIDES, α-PHENYLAZO HYDROPEROXIDES

3836. Tetrakis(pentafluorophenyl)titanium

[37759-21-0] **$C_{24}F_{20}Ti$**



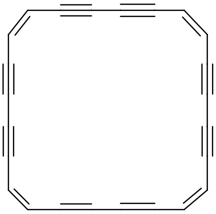
Houben-Weyl, 1975, Vol. 13.3, 300

It explodes at 120—130°C.

See other HALO-ARYLMETALS

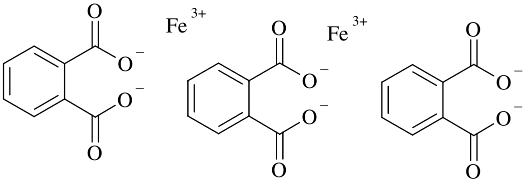
3837. 1,7,13,19-Cyclotetracosatetraene-3,5,9,11,15,17,21,23-octayne (Octahydro[24]-annulene)

[30047-26-8] **$C_{24}H_8$**



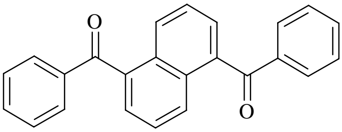
Diederich, F. *et al., Angew. Chem. (Int.)*, 1992, **31**(9), 1101
Explodes on heating.
See other ALKYNES

3838. Iron(III) phthalate
[52118-12-4] **$C_{24}H_{12}Fe_2O_{12}$**



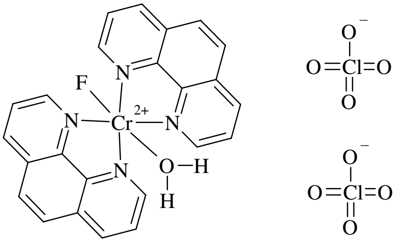
Sulfur compounds
See Phthalic anhydride (reference 2)

3839. 1,5-Dibenzoylnaphthalene
[83-80-7] **$C_{24}H_{16}O_2$**



Preparative hazard
See Aluminium chloride: Benzoyl chloride, etc.

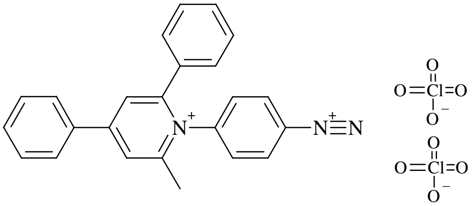
3840. Aquafluorobis(1,10-phenanthroline)chromium(III) perchlorate
[77812-44-3] **$C_{24}H_{18}Cl_2CrFN_4O_{10}$**



Delover, M. *et al., J. Chem. Soc., Dalton Trans.*, 1981, 985
Its explosive properties prevented analysis.
See other AMMINEMETAL OXOSALTS

3841. 1(2′-Diazoniophenyl)2-methyl-4,6-diphenylpyridinium diperchlorate

[55358-25-3] **$C_{24}H_{19}Cl_2N_3O_8$**



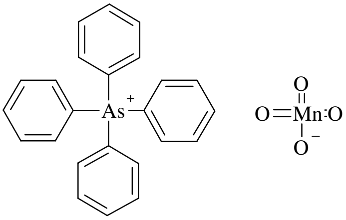
Dorofenko, G. N. *et al., Chem. Abs.*, 1975, **82**, 139908

The title compound, its 3’- and 4’-isomers, and their 2,4,6-triphenyl analogues, exploded on heating.

See other DIAZONIUM PERCHLORATES

3842. Tetraphenylarsonium permanganate

[4312-28-1] **$C_{24}H_{20}AsMnO_4$**

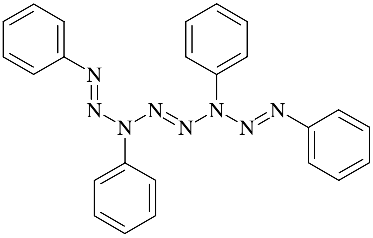


It explodes at 120—130°C.

See entry QUATERNARY OXIDANTS

3843. 1,3,6,8-Tetraphenyloctaazatriene

[ ] **$C_{24}H_{20}N_8$**



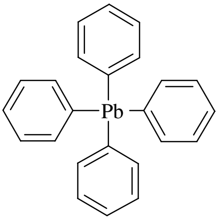
Wohl, A. *et al., Ber.*, 1900, **33**, 2741

This compound (and several *C*-homologues) is unstable and explodes sharply on heating, impact or friction. In a sealed tube, the explosion is violent.

See other HIGH-NITROGEN COMPOUNDS

3844. Tetraphenyllead

[595-89-1] **$C_{24}H_{20}Pb$**



Potassium amide

See Potassium amide: Tetraphenyllead

Sulfur

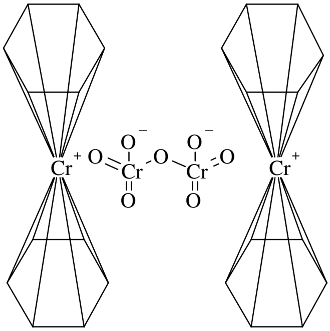
Houben-Weyl, 1975, Vol. 13.3, 236

Interaction may be explosive.

See other ARYLMETALS

3845. Bis(benzene)chromium dichromate

[ ] **$C_{24}H_{24}Cr_4O_7$**



Anon., *Chem. Eng. News*, 1964, **42**(38), 55

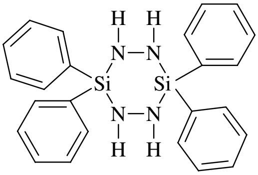
This catalyst exists as explosive orange-red crystals.

See other ORGANOMETALLICS

See related METAL OXOMETALLATES

3846. 3,3,6,6-Tetraphenylhexahydro-3,6-disilatetrazine

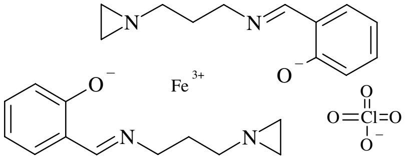
[13272-05-4] **$C_{24}H_{24}N_4Si_2$**



See entry SILYLHYDRAZINES

3847. Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate

[79151-63-6] **$C_{24}H_{30}ClFeN_4O_6$**



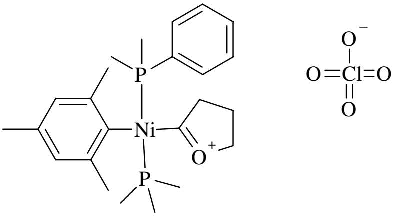
Federer, W. D. *et al., Inorg. Chem.*, 1984, **23**, 3863

Heat- and mildly shock-sensitive, a sample of the complex exploded after hand-grinding in a mortar for 30 min.

See other AMMINEMETAL OXOSALTS, AZIRIDINES

3848. 2-Tetrahydrofuranylidene(dimethylphenylphosphine-trimethylphosphine)-2,4,6-trimethylphenylnickel perchlorate

[ ] **$C_{24}H_{37}ClNiO_5P_2$**



Wada, M. *et al., J. Chem. Soc., Dalton Trans.*, 1982, 794

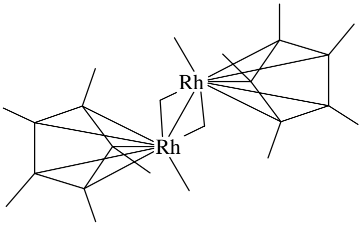
It explodes on heating, like a tetrahydropyranylidene analogue.

See other ORGANOMETALLIC PERCHLORATES

See related ALKYLPHOSPHINES

3849. Di-*μ*-methylenebis(methylpentamethylcyclopentadienyl)dirhodium

[80410-45-3] **$C_{24}H_{40}Rh_2$**



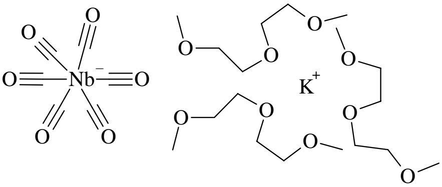
Preparative hazard

See Dichlorodi-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium: Air, Alkylmetals

See related ALKYLMETALS

3850. Tris(bis-2-methoxyethyl ether)potassium hexacarbonylniobate(1—)

[57304-94-6] **$C_{24}H_{42}KNbO_{15}$**



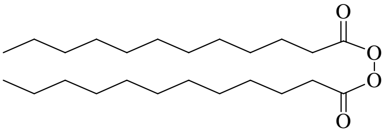
Solvents

Attempts to recover the complex from solutions in solvents other than diglyme led to the formation of pyrophoric solids.

See related CARBONYLMETALS

3851. Didodecanoyl peroxide (Dilauroyl peroxide)

[105-74-8] **$C_{24}H_{46}O_4$**



1. *Haz. Chem. Data*, 1975, 137
2. *CHETAH*, 1990, 183

Though regarded as one of the more stable peroxides, it becomes shock-sensitive on heating, and self-accelerating decomposition sets in at 49°C [1]. One of the more recently calculated values of 46 and 42°C for induction periods of 7 and 60 days, respectively, for critical ignition temperatures is closely similar to that (45°/7 days) previously recorded. Autocatalytic combustion of the polymerisation initiator is exhibited. Although not ordinarily shock sensitive, it responds to a detonator [2].

Charcoal

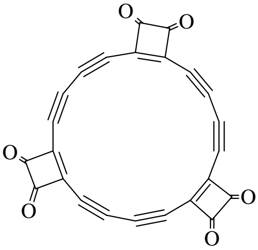
Leleu, *Cahiers*, 1980, (99), 279

Mixtures react exothermally at 90°C, sometimes igniting. (Catalysis by trace metals in the carbon may well be involved).

See other DIACYL PEROXIDES

3852. Tetracyclo[20.2.0.0^{6,9}.0^{14,17}]tetracosa-1(22),6(9),14(17)-triene-2,4,10,12,18,20-hexayne-7,8,15,16,23,24-hexone

[123002-86-8] **$C_{24}O_6$**

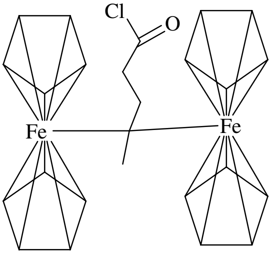


See Oligo(octacarbondioxide)

See other ACETYLENIC COMPOUNDS

3853. 4,4-Diferrocenylpentanoyl chloride

[56386-22-2] **$C_{25}H_{25}ClFe_2O$**



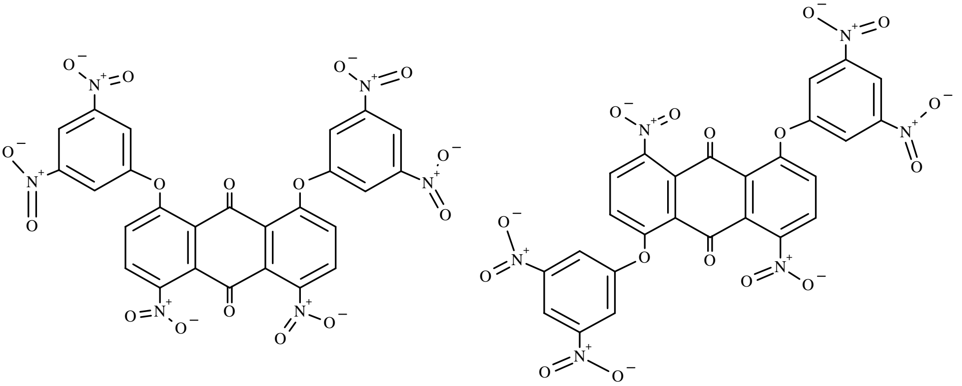
Nielsen, A. T. *et al., J. Org. Chem.*, 1976, **41**, 657

The acid chloride is thermally unstable much above 25°C. At 80—100°C it rapidly evolves hydrogen chloride and forms a black solid.

See other ACYL HALIDES, ORGANOMETALLICS

3854. 1,5-(or 1,8-)Bis(dinitrophenoxy)-4,8-(or 4,5-)dinitroanthraquinone

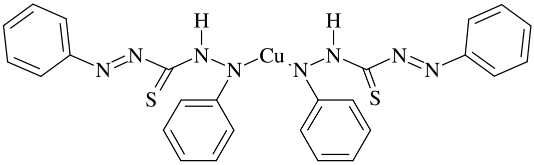
[ ] $C_{26}H_{10}N_6O_{16}$



Fast flame propagation occurs on heating the powders moderately.
See entry HIGH RATE DECOMPOSITION

3855. Copper bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide)

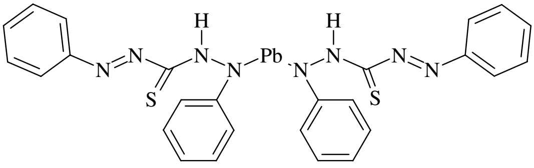
[12213-13-7] $C_{26}H_{22}CuN_8S_2$



Sorbe, 1968, 80
The copper derivative of dithizone explodes at 150°C.
See other N-METAL DERIVATIVES, METAL HYDRAZIDES

3856. Lead bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide)

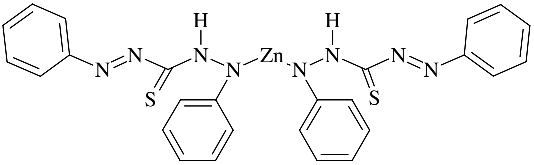
[21519-20-0] $C_{26}H_{22}N_8PbS_2$



Sorbe, 1968, 36
The lead derivative of dithizone explodes at 215°C.
See other N-METAL DERIVATIVES, METAL HYDRAZIDES

3857. Zinc bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide)

[21790-54-5] **$C_{26}H_{22}N_8S_2Zn$**



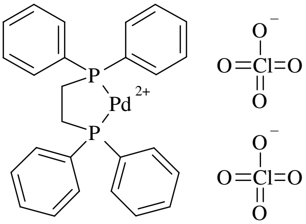
Sorbe, 1968, 159

The zinc derivative of dithizone explodes at 215°C.

See other N-METAL DERIVATIVES, METAL HYDRAZIDES

3858. 1,2-Bis(diphenylphosphino)ethanepalladium(II) perchlorate

[69720-86-1] **$C_{26}H_{24}Cl_2O_8P_2Pd$**



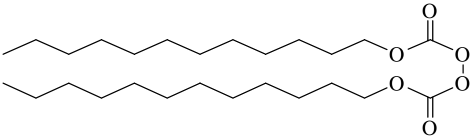
Davies, J. A. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 2246—2249

Extremely sensitive to thermal and mechanical shock, occasionally detonating spontaneously without external stimulus, it should only be prepared and used in solution. The solid is an extreme hazard, and the acetone-solvated complex is also explosive.

See related AMMINEMETAL OXOSALTS

3859. Didodecyl peroxydicarbonate

[24356-04-5] **$C_{26}H_{50}O_6$**



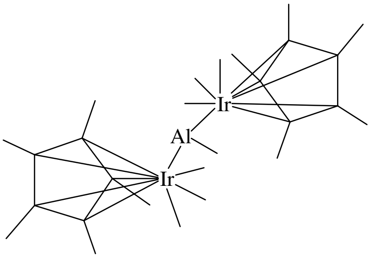
D'Angelo, A. J., US Pat. 3 821 273, 1974

It decomposes violently after 90 min at 40°C, while the hexadecyl homologue is stable for a week at 40°C.

See other PEROXYCARBONATE ESTERS

3860. Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium)

[ ] **$C_{27}H_{51}AlIr_2$**



Isobe, K. *et al., J. Chem. Soc., Dalton Trans.*, 1984, 932

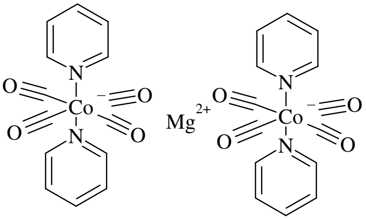
When the complex in pentane at ambient temperature was deliberately exposed to air to produce pentamethylcyclopentadienyltetramethyliridium, it occasionally ignited. Using proper precautions it is not dangerous, but increase in scale above 0.4 mmol is not advised.

See other ORGANOMETALLICS

See related ALKYLMETALS

3861. Tetrakis(pyridine)bis(tetracarbonylcobalt)magnesium

[51006-26-9] **$C_{28}H_{20}Co_2MgN_4O_8$**



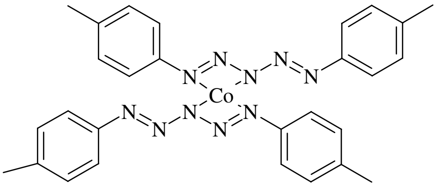
McVicker, G. B., *Inorg. Synth.*, 1976, **16**, 58—59

This, like other transition metal carbonyl derivatives of magnesium, is pyrophoric.

See related CARBONYLMETALS

3862. Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt

[113634-30-3] **$C_{28}H_{28}CoN_{10}$**



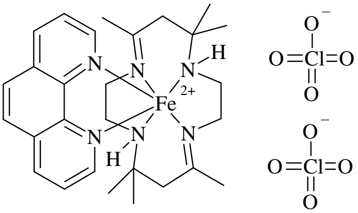
Schmid, R. *et al., Z. Naturforsch. B*, 1987, **42B**, 911—916

The red complex is explosive.

See other HEAVY METAL DERIVATIVES, HIGH-NITROGEN COMPOUNDS, N-METAL DERIVATIVES, PENTAAZADIENES

3863. 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraaza-4,11,-cyclotetradecadiene-1,10-phenanthrolineiron(II) perchlorate

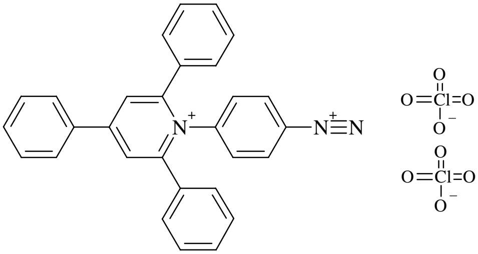
[36732-77-1] **$C_{28}H_{40}Cl_2FeN_6O_8$**



See entry [14] DIENE-N_4 COMPLEXES

3864a. 1(2′-, 3′-, or 4′-Diazoniophenyl)-2,4,6-triphenylpyridinium diperchlorate

[55358-23-1, 55358-29-7, 55358-33-3, resp.] **$C_{29}H_{21}Cl_2N_3O_8$**



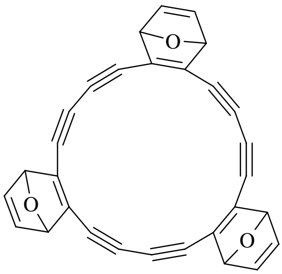
Dorofenko, G. N. *et al., Chem. Abs.*, 1975, **82**, 139908

The three diazonium perchlorate isomers, and their 2-methyl-4,6-diphenyl analogues, all exploded on heating.

See other DIAZONIUM PERCHLORATES

3864b. Trioxaheptacyclotritriacontahexaenehexayne (5,6,7,8,13,14,15,16,21,22,23,24-Dodecadehydro-1,4,9,12,17,20-hexahydro-1,4:9,12:17,20-triepoxytribenzo[*a,g,m*]cyclooctadecene)

[261901-50-2] **$C_{30}H_{12}O_3$**

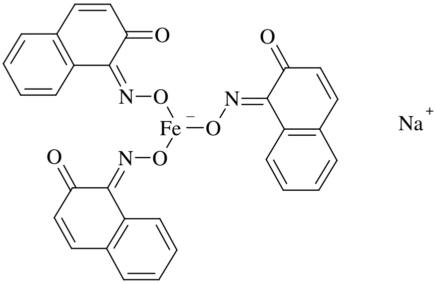


Tobe, Y. *et al., J. Amer. Chem. Soc.*, 2000, **122**(8), 1762

This intermediate, from which it was hoped to prepare [18] annulene, exploded mildly on scratching with a spatula.

See other ACETYLENIC COMPOUNDS

3865. Sodium tris(*O,O′*-1-oximatonaphthalene-1,2-dione)ferrate (Pigment green B)
[16143-80-9] $C_{30}H_{18}FeN_3NaO_6$



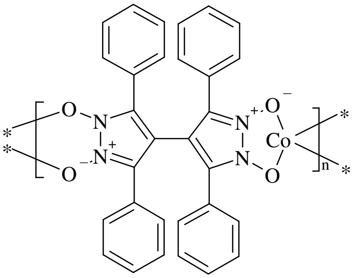
Piotrowski, T., *Chem. Abs.*, 1983, **99**, 159938

The pigment (containing below 1% of inorganic salts) may ignite or explode during milling or drying. The causes of ignition and impact sensitivity were determined and safe handling procedures are proposed.

See other N—O COMPOUNDS

See related OXIMES

3866. Cobalt(II) chelate of bi(1-hydroxy-3,5-diphenylpyrazol-4-yl *N*-oxide)
[75027-71-3] $C_{30}H_{20}CoN_4O_4$



Battei, R. S. *et al., J. Inorg. Nucl. Chem.*, 1980, **42**, 494

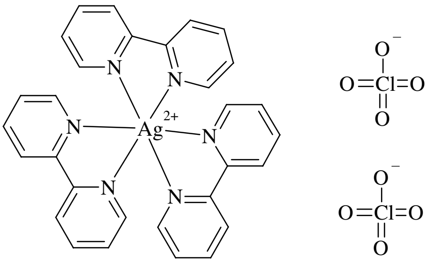
The title cobalt chelate exploded at 175°C during DTA studies, 30° lower than the Co chelate of ‘dicupferron’.

See Cobalt(II) chelate of 1,3-bis(*N*-nitrosohydroxylamino)benzene

See other N—O COMPOUNDS, N-OXIDES

3867. Tris(2,2′-bipyridine)silver(II) perchlorate

[ ] **$C_{30}H_{24}AgCl_2N_6O_8$**



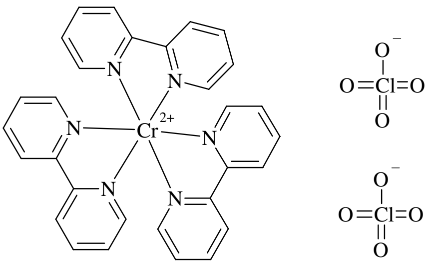
Morgan, G. T. *et al., J. Chem. Soc.*, 1930, 2594

It explodes on heating.

See other AMMINEMETAL OXOSALTS

3868. Tris(2,2′-bipyridine)chromium(II) perchlorate

[15388-46-2] **$C_{30}H_{24}Cl_2CrN_6O_8$**



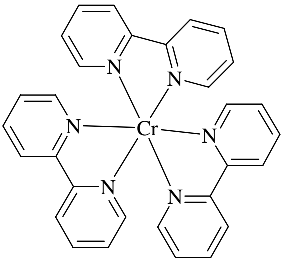
Holah, D. G. *et al., Inorg. Synth.*, 1967, **10**, 34

It explodes violently on slow heating to 250°C and can be initiated by static sparks, but not apparently by impact.

See other AMMINEMETAL OXOSALTS, STATIC INITIATION INCIDENTS

3869a. Tris(2,2′-bipyridine)chromium(0)

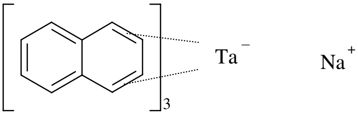
[14751-89-4] **$C_{30}H_{24}CrN_6$**



Herzog, S. *et al., Z. Naturforsch. B*, 1957, **12B**, 809

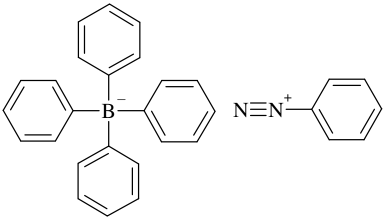
It ignites in air.
See other PYROPHORIC MATERIALS

3869b. Sodium tris(η^4 naphthalene)tantalate(1-) [469873-34-5] 1:1THF complex $C_{30}H_{24}NaTa$



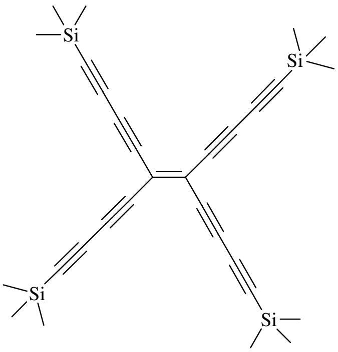
Brennessel, W. W. *et al., J. Amer. Chem. Soc.*, 2002, **124**(35), 10258
Pyrophoric, and spontaneously ignites with fluorocarbon solvents even under argon.
See also METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS
See other ORGANOMETALLICS

3870a. Benzenediazonium tetraphenylborate [2200-13-7] $C_{30}H_{25}BN_2$



Sakakura, T. *et al., J. Chem. Soc., Perk. Trans. 1,* 1994, (3), 283
On two occasions this salt exploded during drying. The dry material is dangerous to handle. In view of the high molecular weight, the diazonium function, alone, represents a low energy per unit mass for explosivity.
See other DIAZONIUM SALTS

3870b. 1,10-Bis(trimethylsilyl)-5.6-bis(trimethylsilylbutadiynyl)dec-5-en-1,3,7,9-tetrayne (Tetrakis(trimethylsilylbutadiynyl)ethene) [ ] $C_{30}H_{36}Si_4$



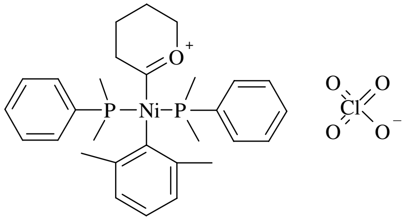
Ozawa, T. *et al., Chemistry Lett.*, 2004, **33**(9), 1180

Since the parent *H*-capped compound was thought capable of detonation, this protected and supposedly stabilised derivative was isolated. A slow decomposition with light emission was remarked while handling it, caution and screens are recommended in handling it.

See other ACETYLENIC COMPOUNDS

3871a. 2-Tetrahydropyranylidene-bis(dimethylphenylphosphine)-3,4,6-trimethylphenyl-nickel perchlorate

[82647-51-6] **$C_{30}H_{41}ClNiO_5P_2$**



Wada, M. *et al., J. Chem. Soc., Dalton Trans.*, 1982, 794

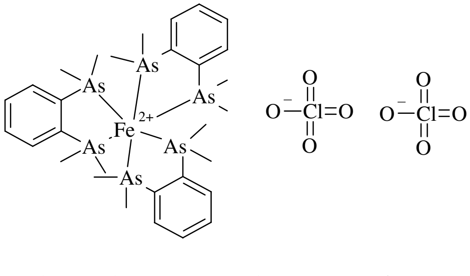
It explodes on heating, like a tetrahydrofuranylidene analogue.

See other ORGANOMETALLIC PERCHLORATES

See related ALKYLPHOSPHINES

3871b. Tris[o-phenylenebis(dimethylarsine)]iron(2+) perchlorate

[21148-13-0] **$C_{30}H_{48}As_6Cl_2FeO_8$**



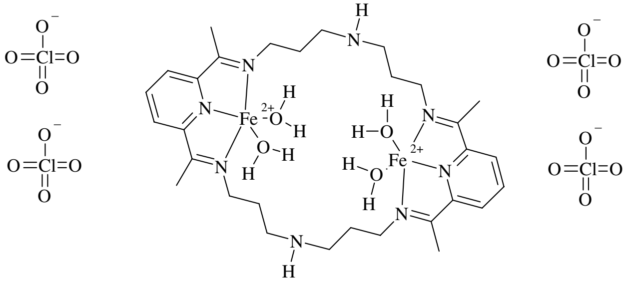
La Pensee, A. A. *et al., J. Chem. Soc. Dalt.*, 2002, (16), 3241

A sample of this complex exploded when touched with a spatula.

See other METAL PERCHLORATES

3872. 2,12,18,28-Tetramethyl-3,7,11,19,23,27,33,34-octaazatricyclo[27.3.1.1(13,17)]-tetratriaconta-1(33),2,11,13,15,17(34)18,27,29,31-decaenetetraaquadiiron(II) tetraperchlorate

[94643-57-9] **$C_{30}H_{52}Cl_4Fe_2N_8O_{20}$**



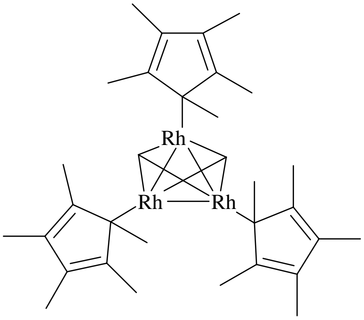
Cabral, M. F. *et al., Inorg. Chim. Acta*, 1984, **90**, 170

The dinuclear complex exploded readily on slight friction.

See other POLYAZACAGED METAL PERCHLORATES

3873. Bis(μ_3-methylidyne)*triangulo*tris(pentamethylcyclopentadienylrhodium)

[83350-11-2] **$C_{32}H_{47}Rh_3$**



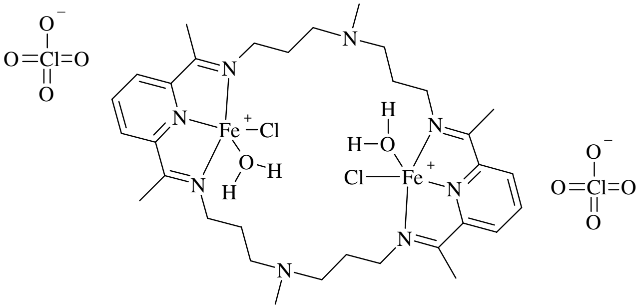
Vasquez de Miguel, A. *et al., Organometallics*, 1982, **1**, 1606

Preparation of hexamethyldialuminium in benzene, necessary for reaction with $(C_5H_5Rh)_2Cl_4$ to give the title compound, is hazardous and should only be attempted by experienced workers.

See other ORGANOMETALLICS

3874. 2,7,12,18,23,28-Hexamethyl-3,7,11,19,23,27,33,34-octaazatricyclo[27.3.1.1-(13,17)]tetratriaconta-1(33),2,11,13,15,17(34),18,27,29,31-decaenediaquadichlorodiiron(II) diperchlorate

[94643-57-9] **$C_{32}H_{52}Cl_4Fe_2N_8O_{10}$**



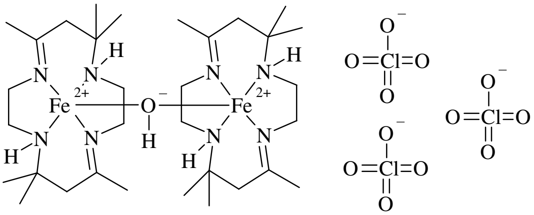
Cabral, M. F. *et al., Inorg. Chim. Acta*, 1984, **90**, 170

The dinuclear complex exploded readily on slight friction.

See other POLYAZACAGED METAL PERCHLORATES

3875. Hydroxobis[5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] triperchlorate

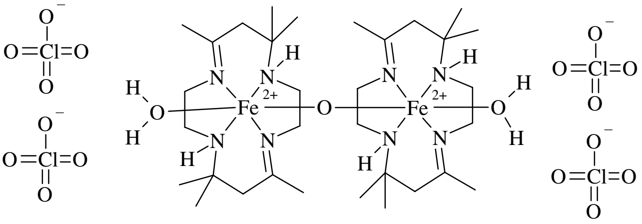
[36913-76-5] **$C_{32}H_{65}Cl_3Fe_2N_8O_{13}$**



See other [14] DIENE-N_4 COMPLEXES

3876. Oxybis[aqua-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] tetraperchlorate

[36841-23-3] **$C_{32}H_{68}Cl_4Fe_2N_8O_{19}$**



See other [14] DIENE-N_4 COMPLEXES

3877. Tetrakis(μ_3-2-amino-2-methylpropanolato)tetrakis(μ_2-2.amino-2-methylpropanolato)hexacopper(II) perchlorate

[100113-85-7] **$C_{32}H_{80}Cl_4Cu_6O_{24}$**

Complex Structure

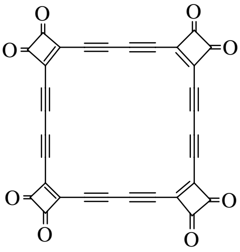
Muhonen, H. *et al., Inorg. Chem.*, 1986, **25**, 800

The complex, containing a bicapped cubane Cu_6O_8 cluster, may explode if heated when dry.

See other AMMINEMETAL OXOSALTS

3878. Octacarbondioxide tetramer

[123002-87-9] **$C_{32}O_8$**

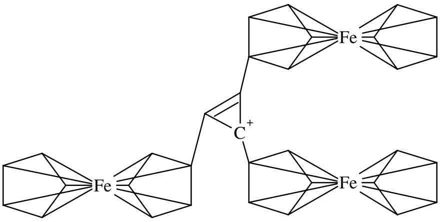


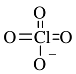
See Oligo(octacarbondioxide)

See other ACETYLENIC COMPOUNDS

3879. Triferrocenylcyclopropenium perchlorate

[56581-58-9] **$C_{33}H_{27}ClFe_3O_4$**





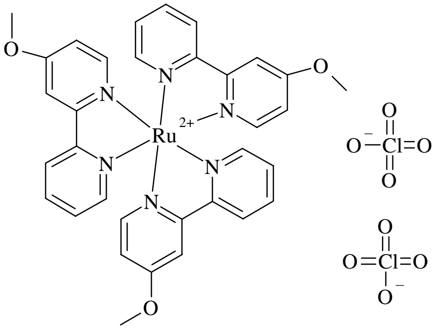
Agranat, I. *et al., Tetrahedron*, 1979, **35**, 738

The salt is thermally stable below 171°C, but may explode on friction at ambient temperature.

See other FRICTIONAL INITIATION INCIDENTS, NON-METAL PERCHLORATES

3880a. Tris(4-methoxy-2,2″bipyridine)ruthenium(II) perchlorate

[ ] **$C_{33}H_{30}Cl_2N_6O_{11}Ru$**



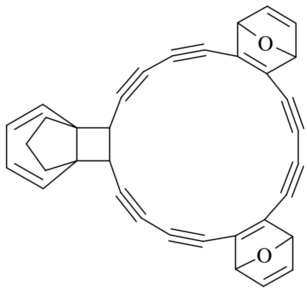
Thomas, R. N., *Univ. Safety Assoc. Safety News*, 1981, **15**, 16—17

Failure of the product (0.5 g) to crystallise out from the aqueous DMF reaction liquor led to vacuum evaporation of the solution at 60—70°C. During evaporation the mixture exploded violently, shattering the fume cupboard sash of toughened glass. The product may well be thermally unstable, but reaction of DMF with excess warm perchloric acid, possibly in near-absence of water, may also have been involved.

See other AMMINEMETAL OXOSALTS

3880b. Dioxaoctacyclopentatriacontaheptaenehexayne

[175655-57-9] **$C_{35}H_{18}O_2$**



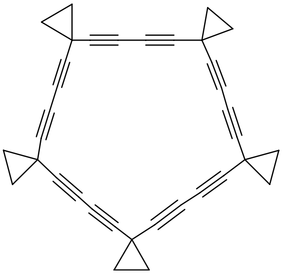
Tobe, Y. *et al., J. Amer. Chem. Soc.*, 2000, **122**(8), 1762

This intermediate, from which it was hoped to prepare [18] annulene, exploded mildly on scratching with a spatula.

See other ACETYLENIC COMPOUNDS

3881. Pentaspiro[2.4.2.4.2.4.2.4.2.4]pentatriaconta-4,6,11,13,18,20,25,27,32,34-decayne

[164077-35-4] **$C_{35}H_{20}$**



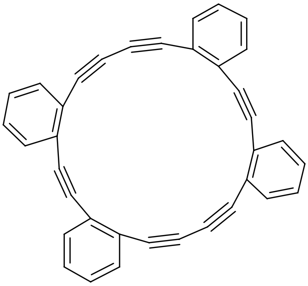
de Meijere, A. *et al., Chem. Eur. J.* 1995, **1**(2), 124

Like others of the series, it is explosive. A sample destroyed the apparatus during melting point determination.

See other ROTANES

3882. 1,2:5,6:11,12:15,16-Tetrabenzocycloconta-1,5,11,15-tetraene-3,7,9,13,17,19-hexayne (1,2:5,6:11,12:15,16-Tetrabenzo-3,7,9,13,17,19-hexahydro[20]annulene)

[ ] **$C_{36}H_{16}$**



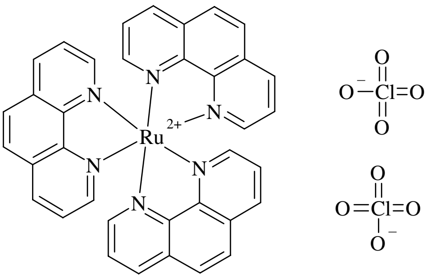
Matzger, A. J. *et al., J. Amer. Chem. Soc.*, 1997, **119**, 2052

Explodes at 245°C to give various forms of carbon, hydrogen and methane and 1 kJ/g of heat.

See other ACETYLENIC COMPOUNDS

3883. Tris(1,10-phenanthroline)ruthenium(II) perchlorate

[27778-27-4] **$C_{36}H_{24}Cl_2N_6O_8Ru$**



Sulfuric acid

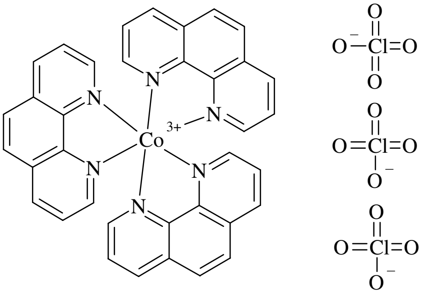
Gillard, R. D. *et al., J. Chem. Soc., Dalton Trans.*, 1974, 1235

Dissolution of the salt in the conc. acid must be very slow with ice-cooling to prevent an explosive reaction.

See other AMMINEMETAL OXOSALTS

3884. Tris(1,10-phenanthroline)cobalt(III) perchlorate

[14516-66-6] **$C_{36}H_{24}Cl_3CoN_6O_{12}$**



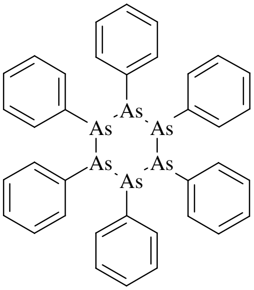
1. Hunt, H. R., *J. Chem. Educ.*, 1977, **54**, 710
2. Kildall, L. K., *J. Chem. Educ.*, 1978, **55**, 476
3. Hunt, H. R., *J. Chem. Educ.*, 1978, **55**, 476

The use of the perchlorate anion to precipitate the cobalt complex to determine the yield [1] is deprecated on the grounds of potential hazard [2], though it was not found possible to cause the salt to detonate by pounding, but it will burn if ignited. A spectroscopic assay method is suggested as an alternative to precipitation [3].

See other AMMINEMETAL OXOSALTS

3885. Hexaphenylhexaarsane

[20738-31-2] **$C_{36}H_{30}As_4$**



Oxygen

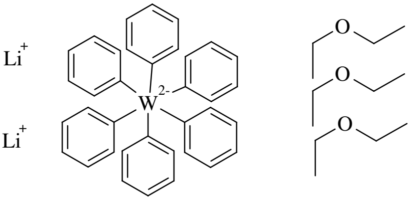
1. Maschmann, E., *Ber.*, 1926, **59**, 1143
2. Blicke, F. F. *et al., J. Amer. Chem. Soc.*, 1930, **52**, 2946—2950

The explosively violent reaction of trimeric 'arsenobenzene' with oxygen [1] was later ascribed to the presence of various catalytic impurities, because the pure compound is stable towards oxygen [2].

See related ALKYLNON-METALS

3886. Lithium hexaphenyltungstate(2—)

[ ] **$C_{36}H_{30}Li_2W$**



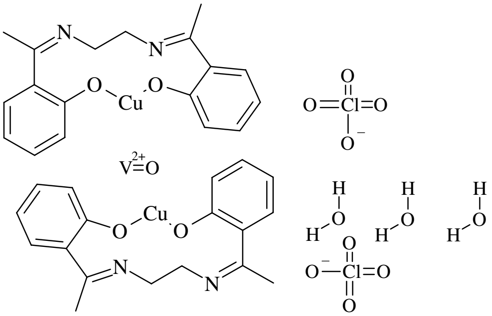
Sarry, B. *et al., Z. Anorg. Chem.*, 1964, **329**, 218

The trietherate is pyrophoric in air.

See related ARYLMETALS

3887. Di[*N,N′*-Ethylenebis(2-oxidoacetophenoneiminato)copper(II)] oxovanadium(IV) diperchlorate

[93895-68-2] **$C_{36}H_{36}Cl_2Cu_2N_4O_{13}V.3H_2O.½EtNO_2$**



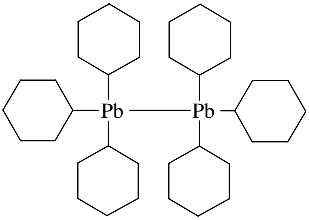
Bencini, A. *et al., Inorg. Chem.*, 1985, **24**, 696

It is thermally unstable and may easily explode.

See related AMMINEMETAL OXOSALTS

3888. Hexacyclohexyldilead

[6713-82-2] **$C_{36}H_{66}Pb_2$**



Halocarbons

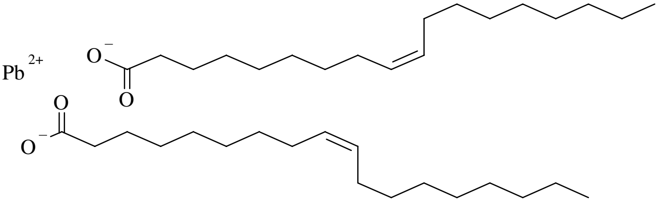
Houben-Weyl, 1975, Vol. 13.3, 168

In absence of other solvent and in presence of air, interaction with carbon tetrabromide is explosive, and with hexabromoethane, more so.

See related ALKYLMETALS

3889. Lead oleate

[1120-46-3] **$C_{36}H_{66}O_4Pb$**



Mineral oil

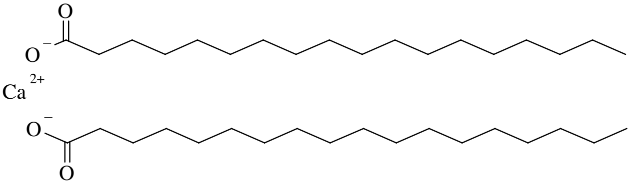
Williams, C. G., *Mech. Eng.*, 1932, **54**, 128—129

Lead oleate greases tend to cause violent explosions when used on hot-running bearings. The cause is not immediately apparent, but peroxidation may well have been involved.

See other HEAVY METAL DERIVATIVES

3890. Calcium stearate

[1592-23-0] **$C_{36}H_{70}CaO_4$**



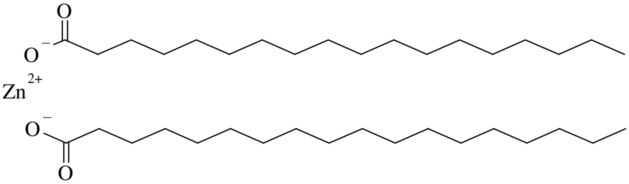
1. Schmutzler, G. *et al., Plaste Kaut.*, 1967, **14**, 827—829
2. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74

Dust explosions and spontaneous ignition hazards for calcium stearate and related plastics additives are detailed and discussed [1]. A maximum pressure increase of 6.6 bar and a maximum rate of rise above 680 bar/s have been recorded [2].

See other AUTOIGNITION INCIDENTS, DUST EXPLOSION INCIDENTS

3891. Zinc stearate

[557-05-1] **$C_{36}H_{70}O_4Zn$**

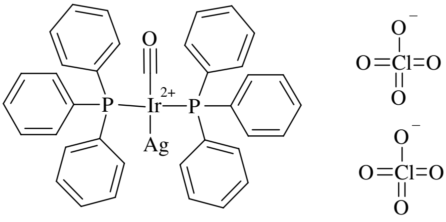


The finely powdered soap is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

3892. Carbonyl-bis(triphenylphosphine)iridium—silver diperchlorate

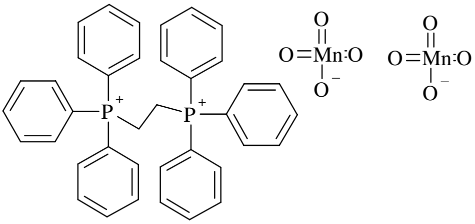
[ ] **$C_{37}H_{30}AgCl_2IrO_9P_2$**



Kuyper, J. *et al., J. Organomet. Chem.*, 1976, **107**, 130
Highly explosive, detonated by heat or shock.
See related AMMINEMETAL OXOSALTS

3893a. 1,2-Bis(triphenylphosphonio)ethane permanganate

[76710-76-4] **$C_{38}H_{34}Mn_2O_8P_2$**



It explodes at 80—90°C.
See entry QUATERNARY OXIDANTS

3893b. Dicopper(I) 1,3,5,7,9,11,13,15,17,19,21,23,25,27,29,31,33,35,37,39,-tetracontaeicosayne-1,40-diide

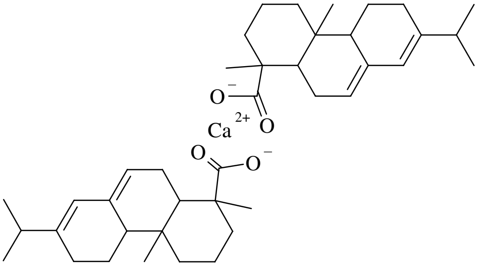
[215310-44-4] **$CuC_{40}Cu$**

$CuC_{40}Cu$

Cataldo, F., *Eur. J. Solid State Inorg. Chem.*, 1998, **35**(3), 81
The ultimate product obtained by oxidising cuprous acetylide could be formulated thus. Although infrared suggested a cumulene structure, not that shown above, it retains the hazards of its progenitor.
See Dicopper(I) acetylide
See other METAL ACETYLIDES

3894. Calcium abietate

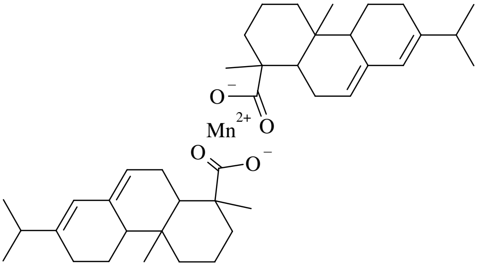
[13463-98-4] **$C_{40}H_{58}CaO_4$**



See entry METAL ABIETATES

3895. Manganese abietate

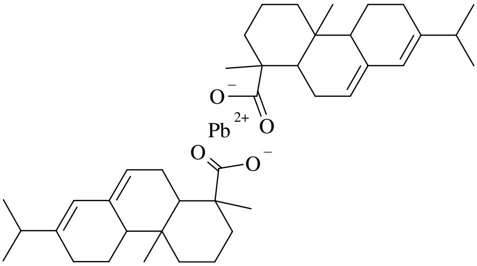
[54675-76-2] **$C_{40}H_{58}MnO_4$**



See entry METAL ABIETATES

3896. Lead abietate

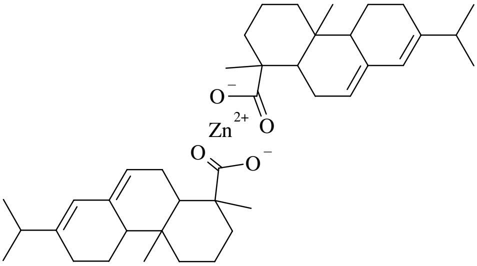
[5434-72-0] **$C_{40}H_{58}O_4Pb$**



See entry METAL ABIETATES

3897. Zinc abietate

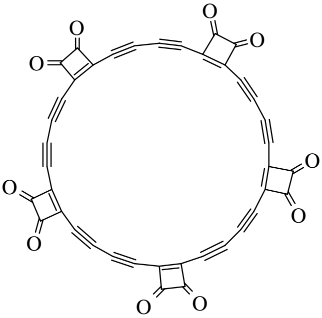
[6798-76-1] **$C_{40}H_{58}O_4Zn$**



See entry METAL ABIETATES

3898. (Octacarbondioxide) pentamer

[ ] **$C_{40}O_{10}$**

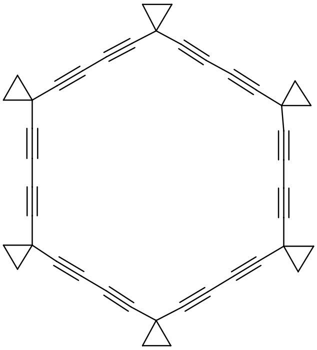


See Oligo(octacarbondioxide)

See other ACETYLENIC COMPOUNDS

3899. Hexaspiro[2.4.2.4.2.4.2.4.2.4.2.4]dotetraconta-4,6,11,13,18,20,25,27,32,34,39,41-dodecayne

[155797-52-7] **$C_{42}H_{24}$**



1. de Meijere, A. *et al., Angew. Chem. (Int.)*, 1994, **33**(8), 869
2. de Meijere, A. *et al., Chem. Eur. J.* 1995, **1**(2), 124

The white solid explodes on friction or impact (photo on the cover of this *Angewandte*) and decomposes at 130°C. The instability is associated with the cyclopropane rings as it is claimed to be absent from the dodecamethyl homologue [1]. Calculation indicates 6 kJ/g available energy [2].

See other ACETYLENIC COMPOUNDS, ROTANES, STRAINED-RING COMPOUNDS

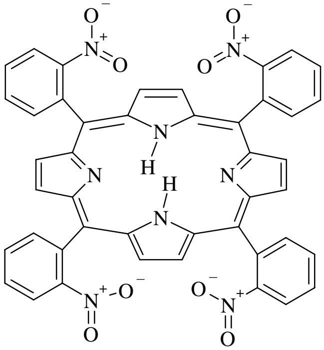
3900. Hexakis(pyridine)iron(II) tridecacarbonyltetraferrate(2—)

[23129-50-2] **$C_{43}H_{30}Fe_5N_6O_{13}$**

Complex Structure

Brauer, 1965, Vol. 2, 1758
Extremely pyrophoric in air.
See related AMMINEMETAL OXOSALTS, CARBONYLMETALS

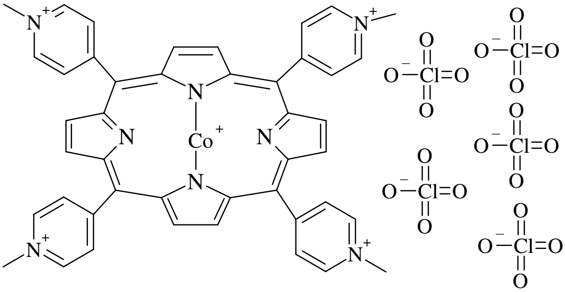
3901. 5,10,15,20-Tetrakis(2-nitrophenyl)porphine
[37116-82-8] **$C_{44}H_{26}N_8O_8$**



Preparative hazard

See 2-Nitrobenzaldehyde: Pyrrole
See other NITROARYL COMPOUNDS

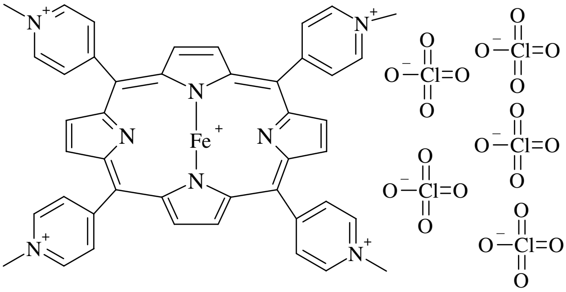
3902. Tetrakis(4-*N*-methylpyridinio)porphinecobalt(III)(5+) perchlorate
[53149-77-2] **$C_{44}H_{36}Cl_5CoN_8O_{20}$**



Pasternack, R. F. *et al., J. Inorg. Nucl. Chem.*, 1974, **36**, 600
A sample obtained by precipitation exploded.
See other AMMINEMETAL OXOSALTS

3903. Tetrakis(4-*N*-methylpyridinio)porphineiron(III)(5+) perchlorate

[64365-00-0] **$C_{44}H_{36}Cl_5FeN_8O_{20}$**



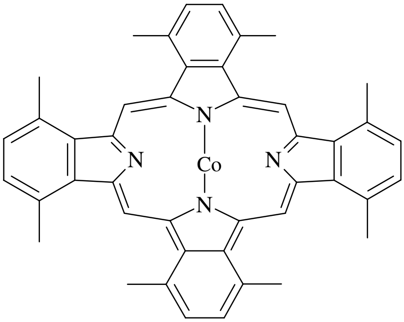
Harris, F. L. *et al., Inorg. Chem.*, 1978, **17**, 71

A small sample exploded when scraped with a metal spatula on a glass frit.

See other AMMINEMETAL OXOSALTS

3904. 1,4,8,11,15,18,22,25-Octamethyl-29*H*,31*H*-tetrabenzo[*b.g.l.q*]porphinato(2—)-cobalt(II)

[27662-34-6] **$C_{44}H_{36}N_4Co$**

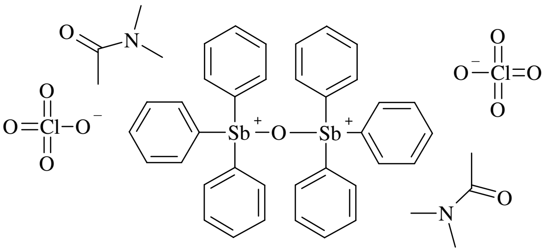


Preparative hazard

See 1,3,4,7-Tetramethylisoindole: Cobalt

3905. Oxybis(*N,N*-dimethylacetamidetriphenylstibonium) perchlorate

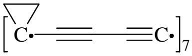
[37035-60-2] **$C_{44}H_{50}Cl_2N_2O_{11}Sb_2$**



Goel, R. G. *et al., Inorg. Chem.*, 1972, **11**, 2143
It exploded on several occasions during handling and attempted analysis.
See related AMMINEMETAL OXOSALTS

3906. Heptaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4]nonatetraconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48-tetradecayne

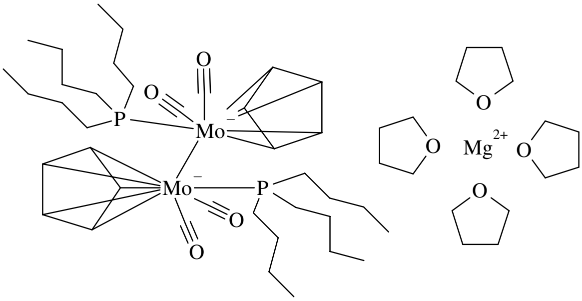
[168848-73-5] **$C_{49}H_{28}$**



See other ROTANES

3907. Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum] — tetrakis(tetrahydrofuran)magnesium

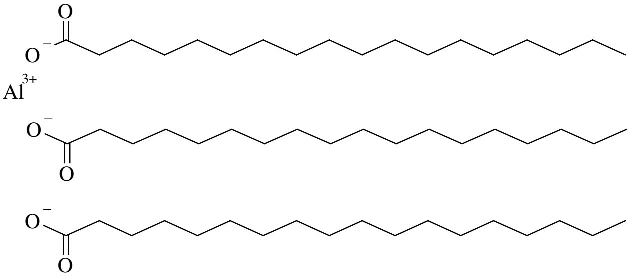
[82148-84-3] **$C_{54}H_{96}MgMo_2O_8P_2$**



McVicker, G. B., *Inorg. Synth.*, 1976, **16**, 59—61
This and other transition metal carbonyl derivatives of magnesium is pyrophoric.
See other ORGANOMETALLICS
See related CARBONYLMETALS

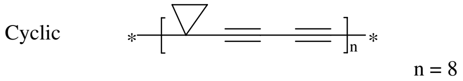
3908. Aluminium stearate

[637-12-7] **$C_{54}H_{105}AlO_6$**



The finely powdered soap is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

3909. Octaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]hexapentaconta-4,6,11,13,18,20,25,27,-32,34,39,41,46,48,53,55-hexadecayne
[164077-36-5] **$C_{56}H_{32}$**



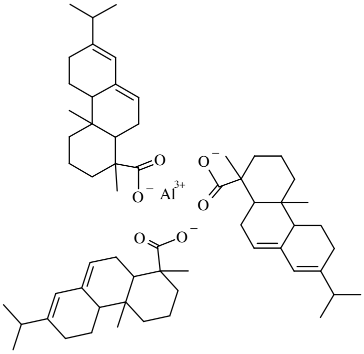
See other ROTANES

3910. Buckminsterfullerene
[99685-96-8] **C_{60}**

C_{60}

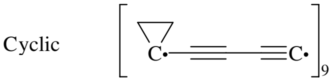
See Carbon

3911. Aluminium abietate
[32454-63-0] **$C_{60}H_{87}AlO_6$**



See entry METAL ABIETATES

3912. Nonaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]trihexaconta-4,6,11,13,18,20,25,27,-32,39,41,46,48,53,55,60,62-octadecayne
[155797-58-3] **$C_{63}H_{36}$**



See other ROTANES

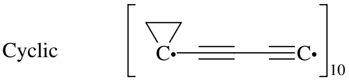
3913. Fullerene
[ ] **C_{70}**

C_{70}

See Carbon

3914. Decaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]heptaconta-4,6,11,13,18,20,25,-27,32,39,41,46,48,53,55,60,62,67,69-eicosayne

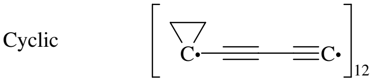
[168848-75-7] **$C_{70}H_{40}$**



See other ROTANES

3915a. Dodecaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]tetraoctaconta-4,6,11,-13,18,20,25,27,32,39,41,46,48,53,55,60,62,67,69,74,76,81,83-tetracosayne

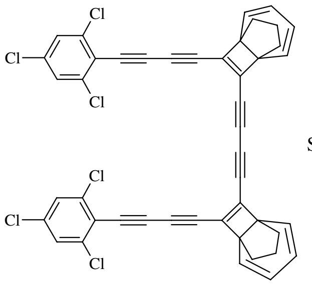
[168848-76-8] **$C_{84}H_{48}$**



See other ROTANES

3915b. [4.3.2]Propellatriene fused Hexachloro[16.16.16]cyclophaneoctadecaynehexaene (*systematic name too long to accomodate*)

[351014-13-6] **$C_{114}H_{60}Cl_6$**



Part structure only:

Similar bridges between vacant 3,3' and 5,5' sites of chlorobenzene rings

Tobe, Y. *et al., Tetrahedron*, 2001, **57**(17), 3629
This intermediate towards rational fullerene synthesis decomposed violently on scratching with a spatula. The unchlorinated equivalent was stable.
See other ACETYLENIC COMPOUNDS

3916. Calcium

[7440-70-2] **Ca**

Ca

FPA H121, 1983; *HCS 1980*, 262

'Product Information Sheet No. 212', Sandwich, Pfizer Chemicals, 1969
Calcium is pyrophoric when finely divided.
See other PYROPHORIC METALS

Alkalies
Merck, 1983, 227
Interaction with alkali-metal hydroxides or carbonates may be explosive.

Ammonia
1. Partington, 1967, 369
2. Gibson, 1969, 369

At ambient temperature, ammonia gas reacts exothermally with calcium, but if warmed the latter becomes incandescent [1]. The metal dissolves unchanged in liquid ammonia, but if the latter evaporates, the finely divided metal is pyrophoric [2].
See other PYROPHORIC METALS

Asbestos cement
Scott, P. J., *School Sci. Rev.*, 1967, **49**(167), 252
Drops of molten calcium falling on to hard asbestos cement sheeting caused a violent explosion which perforated the sheet. Interaction with sorbed water seems likely to have occurred.
See Water, below

Carbon dioxide, Nitrogen
See Carbon dioxide: Metals, Nitrogen

Chlorine fluorides
See Chlorine trifluoride: Metals
Chlorine pentafluoride: Metals

1,2-Diaminoethane
Benkeser, R. A. *et al., Tetrahedron Lett.*, 1984, **25**, 2089—2092
The use of calcium in 1,2-diaminoethane as a safer substitute for sodium or lithium in liquid ammonia for the improved Birch reduction of aromatic hydrocarbons is described in detail.

Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Metals

Halogens MRH Chlorine 7.15/64
Mellor, 1941, Vol. 3, 638
Massive calcium ignites in fluorine at ambient temperature, and finely divided (but not massive) calcium ignites in chlorine.

Lead chloride
Mellor, 1941, Vol. 3, 369
Interaction is explosive on warming.

Mercury
Pascal, 1958, Vol. 4, 290
Amalgam formation at 390°C is violent.

Other reactants
Yoshida, 1980, 98

MRH values calculated for 16 combinations, largely with oxidants, are given.

Phosphorus(V) oxide
See Tetraphosphorus decaoxide: Metals

Silicon
Mellor, 1940, Vol. 6, 176—177
Interaction is violently incandescent above 1050°C after a short delay.

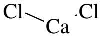
Sodium, Mixed oxides
Anon., *BCISC Quart. Safety Summ.*, 1966, **37**(145), 6
An operator working above the charging hole of a sludge reactor was severely burned when a quantity of burning sludge containing calcium and sodium metals and their oxides was ejected. This very reactive mixture is believed to have been ignited by drops of perspiration falling from the operator.
See Water, below

Sulfur MRH 6.69/44
Mellor, 1941, Vol. 3, 639
A mixture reacts explosively when ignited.

Sulfur, Vanadium(V) oxide
See Vanadium(V) oxide: Calcium, etc.

Water
'Product Information Sheet No. 212', Sandwich, Pfizer Chemicals, 1969
Calcium or its alloys react violently with water (or dilute acids) and the heat of reaction may ignite evolved hydrogen under appropriate contact conditions.
See ASBESTOS CEMENT ABOVE
See other METALS

3917. Calcium chloride
[10043-52-4] **$CaCl_2$**



HCS 1980, 247

Methyl vinyl ether
See Methyl vinyl ether: Acids

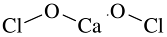
Water
1. *MCA Case History No. 69*
2. *MCA Case History No. 2300*

The exotherm produced by adding solid calcium chloride to hot water caused violent boiling [1], and the same happened 25 years later [2].

Zinc
Anon., *ABCM Quart. Safety Summ.*, 1932, **3**, 35

Prolonged action of calcium chloride solution upon the zinc coating of a galvanised iron vessel caused slow evolution of hydrogen, which became ignited and exploded.
See other CORROSION INCIDENTS, GAS EVOLUTION INCIDENTS, METAL HALIDES

3918. Calcium hypochlorite
[7778-54-3] **$CaCl_2O_2$**



FPA H46, 1976; *HCS 1980*, 269

1. Sidgwick, 1950, 1217
2. Clancey, V. J., *J. Haz. Mat.*, 1975, **1**, 83—94
3. Cave, R. F., *Chem. in Austr.*, 1978, **45**, 313
4. Uehara, Y. *et al., Chem. Abs.*, 1979, **91**, 159834
5. Uehara, Y. *et al., Chem. Abs.*, 1979, **91**, 180693
6. Uehara, Y. *et al., Chem. Abs.*, 1980, **92**, 220207
7. Clancey, V. J., *Hazards of Pressure*, IChE Symp. Ser. No. 102, 11—23, Oxford, Pergamon, 1987
8. Wejtowicz, J. A., *ibid.*, 323—351
9. Rabovskii, B. G. *Chem. Abs.* 2004, **140**, 95850w

This powerful oxidant is technically of great importance for bleaching and sterilisation applications, and contact with reducants or combustible materials must be under controlled conditions. It is present in diluted state in bleaching powder, which is a less powerful oxidant with lower available chlorine content [1]. There have been several instances of mild explosions and/or intense fires on ships carrying cargoes of commercial hypochlorite, usually packed in lacquered steel drums and of Japanese origin. Investigational work was still in progress, but preliminary indications suggested that presence of magnesium oxide in the lime used to prepare the hypochlorite may have led to the presence of magnesium hypochlorite which is known to be of very limited stability. Unlike many other oxidants, the hypochlorite constitutes a hazard in the absence of other combustible materials, because after initiation, local rapid thermal decomposition will spread through the contained mass of hypochlorite as a vigorous fire which *evolves*, rather than consumes, oxygen [2]. Thermal decomposition with evolution of oxygen and chlorine sets in around 175°C and will propagate rapidly through the whole bulk.

Several instances of containers or drums igniting or erupting on reopening after previous use have been reported, and may well have involved formation by slow hydrolysis of a relatively high concentration of dichlorine monoxide in the containers. This may have been caused to decompose from sudden exposure to light, by friction on opening the drum, or by a static spark. In one incident, a dull (gas) explosion was heard immediately before the solid erupted. Dry storage is essential [3]. Extrapolation from small-scale determinations of critical thermal ignition temperatures to commercial dimensions (35.4 or 38.2 cm diameters) gave values of 76.3 and 75°, as compared with experimental values of 77 and 75°C, respectively [4]. Fire and explosion hazards of high strength (70%) calcium hypochlorite were studied, with measurements of thermal properties, ignition temperatures, shock-sensitivity, flame propagation rates and explosive power for mixtures with organic materials [5]. A review of the results, and their comparison with predictions from computer simulation has been published [6]. Further possible causes of the instability of commercial 70% calcium hypochlorite are discussed [7], but it is held that the material, if stored and used correctly, is a relatively stable product in the absence of impurities [8]. The calculated value of 75°C for criticial ignition temperature agrees with the previously recorded value of 76°C. Calculations of 'critical mass' have been attempted [9].

See BLEACHING POWDER

See related FRICTIONAL INITIATION INCIDENTS, IRRADIATION DECOMPOSITION INCIDENTS, STATIC INITIATION INCIDENTS

Acetic acid, Potassium cyanide

Pitt, M. J., private comm., 1984

A jug containing calcium hypochlorite (probably as moist solid) was used as a disposal receptacle for cyanide wastes from student preparations of benzoin. When a little acetic acid residue was inadvertently added, an explosion occurred, attributed to a cyanide—chlorine redox reaction.

See other REDOX REACTIONS

Acetylene

Rüst, 1948, 338

Contact of acetylene with bleaching powder, etc., may lead (as with chlorine itself) to formation of explosive chloroacetylenes. Application of hot water to free a partially frozen acetylene purification system which contained bleaching powder caused a violent explosion to occur.

See related HALOACETYLENE DERIVATIVES

Algaecide

Cave, R. F., *Chem. in Austr.*, 1978, **45**, 314

When algaecide (possibly a conc. solution of a quaternary ammonium salt) was spilt on a drum of swimming pool sterilant, it ignited and flared up immediately.

Ammonium chloride MRH 1.05/27

1. Morris, D. L., *Science Teach.*, 1968, **35**(6), 4
2. Anderson, M. B., *Science Teach.*, 1968, **35**(9), 4
3. Rai, H., *Chem. News*, 1918, **117**, 253

When calcium hypochlorite was inadvertently used in place of calcium hydroxide to prepare ammonia gas, an explosion occurred [1], attributed to formation of nitrogen trichloride [2]; this was early claimed to be one of the most efficent methods of preparing the trichloride [3].

See Nitrogenous bases, below

Calcium carbide

Saville, B. W., 1988, private communication

A mixture explodes violently on addition of a drop of water.

Carbon

Mellor, 1941, Vol. 2, 262

A confined intimate mixture of hypochlorite and finely divided charcoal exploded on heating.

Carbon tetrachloride

491M, 1975, 84

Use of a carbon tetrachloride extinguisher on a fire in an open container of hypochlorite caused a severe explosion.

See Oxygen (Gas): Halocarbons

Contaminants

1. *MCA Case History No. 666*
2. Cave, R. F., *Chem. in Austr.*, 1971, **45**, 314

The contents of a drum erupted and ignited during intermittent use. This was attributed to contamination of the soldered metal scoop (normally kept in the drum) by oil, grease or water, or all three, and subsequent exothermic reaction with the oxidant [1]. Use of a bucket, possibly contaminated with traces of engine oil, to transport the oxidant led to eruption and ignition of the contents [2].

See Iron oxide, below

See Organic matter, below

N,N-Dichloromethylamine

See N,N-Dichloromethylamine: Calcium hypochlorite, etc.

Hydrocarbons

Young, J. A., *CHAS Notes*, 1992, **X**(5), 3

'Gasoline' inflames some minutes after being poured onto the hypochlorite. A fire consequent upon transporting the two in adjacent containers in a car is reported. The editor imagines that non-hydrocarbon fuel additives may also be involved.

See Organic matter, etc., below

Hydroxy compounds MRH values below reference

1. Fawcett, H. H., *Ind. Eng. Chem.*, 1959, **51**(4), 90A
2. Kirkbride, K. P. *et al., J. Forensic Sci.*, 1991, **36**(3), 902
3. MRH values: Glycerol 13/12, phenol 2.26/7, ethanol 2.30/7, methanol 2.34/10

Contact of the solid hypochlorite with glycerol, diethylene glycol monomethyl ether or phenol causes ignition within a few min, accompanied by irritant smoke, especially with phenol (formation of chlorophenols). Ethanol may cause an explosion, as may methanol, undoubtedly owing to formation of the alkyl hypochlorites [1]. Reaction with polyethylene glycol hydraulic fluid may produce ignition, with a fireball. A mechanism for creation of combustible gases is proposed [2].

Iron oxide (rust)

Gill, A. H., *Ind. Eng. Chem.*, 1924, **16**, 577

Presence of rust in metal containers has caused many accidental explosions. Metal oxides catalyse the oxygen-evolving decomposition of the oxidant.

Nitrogenous bases MRH Ethylamine 2.92/15

Kirk-Othmer, 1963, Vol. 2, 105

Primary aliphatic or aromatic amines react with calcium (or sodium) hypochlorite to form *N*-mono- or di-chloroamines which are explosively unstable, but less so than nitrogen trichloride.

Nitromethane MRH 5.69/99+

Fawcett, H. H., *Trans. Nat. Safety Congr. Chem. Fertilizer Ind.*, Vol. 5, 32, Chicago, NSC, 1963

They interact, after a delay, with extreme vigour.

Oil, Polyethylene film, Water, Wood

1. Armstrong, B. S., *Loss Prev. Bull.,* 1988, (084), 25—31
2. Sampson, R. G., private comm., 1989

Impact damage occurred to one of 48 10 kg polypropylene tubs of calcium hypochlorite, each closed with a polythene lid, all supported on a wooden pallet and stretch-wrapped round the base with polyethylene film. The spilled material was swept up and discarded, and the pallet was moved to another part of the warehouse, and some 30 mins. later flames were seen at the base of the pallet [1]. Ignition was attributed to contact between residual solid hypochlorite on the pallet and lubricant drips on the concrete floor from fork lift traffic. Application of a dry powder extinguisher had little effect on the fire, but use of a 40 l water extinguisher led to rapid escalation of the fire as contact between hypochlorite and wood was increased. Flash-over occurred and the fire eventually involved a considerable fraction of the 1400 t of assorted warehouse contents [2].

See Organic matter, etc., below

See other IGNITION SOURCES

Organic matter

1. ‘Halane’ Information Sheet, Wyandotte Chem. Co., Michigan, 1958
2. Weicherz, J., *Chem. Ztg.*, 1928, **52**, 729
3. Cave, R. F., *Chem. in Austr.*, 1978, **45**, 313

Mixtures of the solid hypochlorite with 1% of admixed organic contaminants are sensitive to heat in varying degree. Wood caused ignition at 176°, while oil caused violent explosion at 135°C [1]. When solid hypochlorite was transferred to a bucket which had been cleaned out with an alcoholic cleaning composition, it ignited violently. This could not be repeated, but it was found that many organic liquids and fibrous materials caused ignition if warmed to 100°C with the oxidant [2]. Heating a little solid oxidant in a lightly greased crucible led to violent ignition around 180°C [3].

See reference 5 above; Contaminants, above

See Turpentine, below

Organic matter, Water

1. Tatara, S. *et al.*, Ger. Offen., 2 450 816, 1975
2. Lawrence, S., Internet, 1996

Calcium hypochlorite containing over 60% active chlorine normally ignites in contact with lubricating oils, but addition of 16—22% of water will prevent this.

Examples show the effect of 18% (but not 15%) of added water in preventing ignition when glycerol was dripped onto a hypochlorite (79% active chlorine) containing 2% of oil [1]. Ignition with brake fluid is also reported, in this case reaction is accelerated by cola soft drinks - which are dilute acids rather than just water [2].

Organic sulfur compounds

1. Stephenson, F. G., *Chem. Eng. News*, 1973, **51**(26), 14
2. Laboratory Waste Disposal Manual, 142, Washington, MCA, 1969—1972 edns (withdrawn in 1980)
3. *MCA Guide for Safety in the Chemical Laboratory*, 464, New York, Van Nostrand-Reinhold, 1972
4. *491M*, 1975, 85
5. Wacker, J. V. *et al., Rec. Trav. Chim.*, 1986, **105**(3), 99—107

Contact of the solid oxidant with organic thiols or sulfides may cause a violent reaction and flash fire [1]. This procedure was recommended formerly for treating spills of sulfur compounds [2,3], but is now withdrawn as potentially hazardous. Use of an aqueous solution of up to 15% concentration, or of 5% sodium hypochlorite solution is recommended [1]. Addition of 10 g of oxidant to 5 ml portions of 1-propanethiol or isobutanethiol led to explosions [4]. Application of factorial design techniques to experimental planning gave specific conditions for the safe oxidation of organic sulfides to sulfoxides using calcium hypochlorite or sodium chlorate [5].

See Sulfur, below

Other reactants

Yoshida, 1980, 133

MRH values calculated for 11 combinations with oxidisable materials are given.

Sodium 1,3-dichloro-1,3,5—triazine-2,4-dione-6-oxide

See Sodium 1,3-dichloro-1,3,5—triazine-2,4-dione-6-oxide: Calcium hypochlorite

Sodium hydrogen sulfate, Starch, Sodium carbonate

Anon., *Ind. Eng. Chem. (News Ed.)*, 1937, **15**, 282

Shortly after a mixture of the four ingredients had been compressed into tablets, incandescence and an explosion occurred. This may have been caused by interaction of the oxidant and starch, accelerated by the acid salt, but may also have involved dichlorine monoxide liberated by the same salt.

Sulfur

Katz, S. A. *et al., Chem. Eng. News*, 1965, **46**(29), 6

Admixture of damp sulfur and ‘swimming pool chlorine’ caused a violently exothermic reaction, and ejection of molten sulfur.

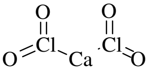
Turpentine

491M, 1975, 85

An explosion occurred soon after the oxidant was put into a can which had contained turpentine but was thought to be empty.

See other METAL HYPOCHLORITES, OXIDANTS

3919. Calcium chlorite
[14674-72-7] **$CaCl_2O_4$**



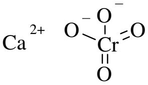
Potassium thiocyanate

Pascal, 1960, Vol. 16, 264

Mixtures may ignite spontaneously.

See other CHLORITE SALTS, METAL OXOHALOGENATES

3920. Calcium chromate
[13816-48-3] **$CaCrO_4$**



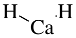
Boron

1. Rogers, J. W. *et al., Energy Res. Abs.*, 1981, **6**, 20813
2. Rogers, J. W., *Proc. 8th Int. Pyrotech. Seminar*, 1982, 556—573

Pyrotechnic properties of blends with 20% boron were studied [1], and the performance of several other blends has been assessed [2].

See other METAL OXOMETALLATES, OXIDANTS

3921. Calcium hydride
[7789-78-8] **CaH_2**



HCS 1980, 268

Halogens

Mellor, 1941, Vol. 16, 651

Heating the hydride strongly with chlorine, bromine or iodine leads to incandescence.

Hexachlorobenzene

Loiselle, S. *et al., Environ. Sci. Technol.* 1997, **31**(1), 261; *J. Solid State Chem.*, 1997, **129**(2), 263

It was discovered that milling hexachlorobenzene with calcium hydride, to effect dechlorination, could give rise to explosive reaction, the conditions under which this happens were studied.

Manganese dioxide

See Manganese(IV) oxide: Calcium hydride

Metal oxohalogenates

MRH values: Ammonium bromate 4.52/82, ammonium chlorate 6.36/76, ammonium perchlorate 6.53/70, barium bromate 3.97/76, barium chlorate 4.85/72, calcium bromate 5.02/70, calcium chlorate 6.53/62, potassium bromate 4.56/73, potassium chlorate 5.81/56, potassium perchlorate 6.07/63, silver chlorate 4.60/73, sodium bromate 4.85/70, sodium chlorate 6.90/63, sodium perchlorate 6.69/60

1. Mellor, 1946, Vol. 3, 651
2. Yoshida, 1980, 214

Mixtures of the hydride with various bromates, chlorates and perchlorates explode on grinding [1]. MRH values calculated for 14 such combinations are given [2].

Other reactants

See next above

Silver halides

Mellor, 1941, Vol. 3, 389, 651

A mixture of silver fluoride and the hydride incandesces on grinding, and the iodide reacts vigorously on heating.

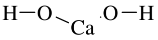
Tetrahydrofuran

See Tetrahydrofuran: Lithium tetrahydroaluminate

See other METAL HYDRIDES

3922. Calcium hydroxide

[1305-62-0] **CaH_2O_2**



Polychlorinated phenols, Potassium nitrate

Kozloski, R. P., *Chem. Eng. News*, 1982, **60**(11), 3

When chlorinated phenols are heated for analytical purposes with calcium hydroxide—potassium nitrate mixtures, chlorinated benzodioxins analogous to the extremely toxic tetrachlorodibenzodioxin may be formed.

Sugars

See SUGARS

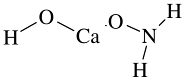
1,3,5-Trinitrohexahydro-1,3,5-triazine

See 1,3,5-Trinitrohexahydro-1,3,5-triazine: Calcium hydroxide, Water

See other INORGANIC BASES

3923. Calcium hydroxide *O*-hydroxylamide

[ ] **CaH_3NO_2**

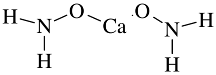


Sorbe, 1968, 43

It explodes on heating (and presumably would be formed if distillation of hydroxylamine from calcium oxide were attempted).
See Hydroxylamine: Metals
See other N—O COMPOUNDS

3924. Calcium bis(*O*-hydroxylamide)

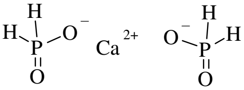
[ ] **$CaH_4N_2O_2$**



See Hydroxylamine: Metals
See other N—O COMPOUNDS

3925. Calcium phosphinate (Calcium hypophosphite)

[7789-79-9] **$CaH_4O_4P_2$**

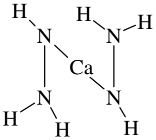


Other reactants
Yoshida, 1980, 344
MRH values calculated for 8 combinations with various reagents are given.

Potassium chlorate MRH 2.88/49
See Potassium chlorate: Reducants
See other METAL PHOSPHINATES, REDUCANTS

3926. Calcium hydrazide

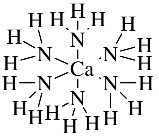
[ ] **CaH_6N_4**



Hydrazine and its Derivatives, Schmidt, F. W., New York, Wiley, 1984, 75
Liable to explode on preparation from the metal, or amide, and hydrazine. Other authors, however, report a 1:1 hydrazide [28330-64-5] as being fairly stable.
See other METAL HYDRAZIDES

3927. Hexaamminecalcium

[12133-31-2] **$CaH_{18}N_6$**

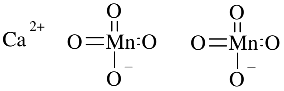


491M, 1975, 83

It ignites in air.
See related N-METAL DERIVATIVES

3928. Calcium permanganate

[10118-76-0] **$CaMn_2O_8$**



Acetic acid,
MRH 2.93/18

Acetic anhydride MRH 3.14/15
See Potassium permanganate: Acetic acid, etc.

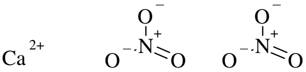
Cellulose
Kirk-Othmer, (3rd ed) 1982, Vol. 19, 494
Calcium permanganate is a more active oxidant than the potassium salt, and ignites paper or cotton on contact.

Hydrogen peroxide MRH 1.59/99+
See Hydrogen peroxide: Metals, etc.

Other reactants
Yoshida, 1980, 92
MRH values calculated for 18 combinations, largely with oxidisable materials, are given.
See other OXIDANTS

3929. Calcium nitrate

[10124-37-5] **CaN_2O_6**



HCS 1980, 270

Aluminium, Ammonium nitrate, MRH Aluminium 9.33/36

Ammonium nitrate, Hydrocarbon oil

Haid, A. *et al., Jahresber. Chem. Tech. Reichsanst.*, 1930, **8**, 108—115

The explosibility of the double salt, calcium ammonium nitrate, is enhanced by presence of oil.

See Ammonium nitrate: Organic fuels

Ammonium nitrate, Water-soluble fuels

Clark, W. F. *et al.*, US Pat. 3 839 107, 1970

Up to, or over 40% of the ammonium nitrate content of explosive mixtures with water-soluble organic fuels may be replaced with advantage by calcium nitrate.

Formamide, Water

1. Wilson, J. F. *et al.*, S. Afr. Pat. 74 03 305, 1974
2. Slykehouse, T. E., Can. Pat. 1 011 561, 1977

A mixture containing 51% of calcium nitrate and 12% ammonium nitrate with 27% formamide and 10% water is detonable at —20°C [1]. Addition of aluminium powder improves performance as a blasting explosive [2].

Organic materials

Sorbe, 1968, 423

Mixtures of the nitrate with organic materials may be explosive.

Other reactants

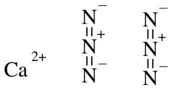
Yoshida, 1980, 193

MRH values calculated for 16 combinations with oxidisable materials are given.

See other METAL NITRATES, OXIDANTS

3930. Calcium azide

[19465-88-4] **CaN_6**



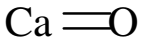
1. Mellor, 1940, Vol. 8, 349
2. Stull, 1977, 10

Calcium, strontium and barium azides are not shock-sensitive, but explode on heating at about 150, 170 and 225 (or 152)°C, respectively. In sealed tubes, the explosion temperatures are higher [1]. Although calcium azide is rather mildly endothermic (ΔH_f° (s) +46 kJ/mol, 0.37 kJ/g), it can decompose much more exothermally to the nitride (189.9 kJ/mol, 1.53 kJ/g) than to the elements [2].

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

3931. Calcium oxide

[1305-78-8] **CaO**



NSC 241, 1982; *HCS 1980*, 272

Ethanol

Keusler, V., *Apparatebau*, 1928, **40**, 88—89

The lime—alcohol residue from preparation of anhydrous alcohol ignited on discharge from the still and caused a vapour explosion. The finely divided and reactive lime may have heated on exposure to atmospheric moisture and caused ignition.

See Water, below

Hydrogen fluoride

See Hydrogen fluoride: Oxides

Interhalogens

See Bromine pentafluoride: Acids, etc.	MRH 3.23/56
Chlorine trifluoride	MRH 4.06/52

Other reactants

Yoshida, 1980, 126

MRH values calculated for 6 combinations with various reagents are given.

Phosphorus(V) oxide

See Tetraphosphorus decaoxide: Inorganic bases

Water

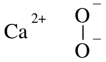
1. Mellor, 1941, Vol, 3, 673
2. Anon., *Fire*, 1935, **28**, 30
3. Amos, T., *Zentr. Zuckerind.*, 1923, **32**, 103
4. Anon., *BCISC Quart. Safety Summ.*, 1967, **38**, 15
5. Anon., *BCISC Quart. Safety Summ.*, 1971, **42**(168), 4
6. Anon., *Engrg. Digest*, 1908, **4**, 661
7. US Government, http://tis.eh. doe.gov/web/oeaf/oe_weekly-2000, 2000-11

Crystalline calcium oxide reacts imperceptibly slowly with water, but the powdered material reacts with explosive violence after a few minutes delay [1]. Quicklime, when mixed with $^1/_3$ its weight of water, will reach 150—300°C (depending on quantity) and may ignite combustible material. Occasionally 800—900°C has been attained [2]. Moisture present in wooden storage bins caused ignition of the latter [3]. After a thunderstorm, straw bales surrounding a 20 ton heap of quicklime pellets under plastic sheet ignited [7]. A water jet was used unsuccessfully to clear a pump hose blocked with quicklime. On standing, the exothermic reaction generated enough steam to clear the blocked hose explosively [4]. Two glass bottles of calcium oxide powder burst while on a laboratory shelf, owing to the considerable increase in bulk which occurs on hydration. Storage in plastic bottles is recommended, and granular oxide should cause fewer problems in this respect than the powder [5]. The powerful expansion effect was formerly used in coal-mining operations [6].

See other GLASS INCIDENTS, INORGANIC BASES, METAL OXIDES

3932. Calcium peroxide

[1305-79-9] **CaO_2**



Chlorinated paraffin

Anon., *Chem. Brit.*, 1997, **33**(6), 7

A fire is reported subsequent to industrial mixing of calcium peroxide and a chlorinated paraffin. Even completely chlorinated hydrocarbons can be oxidised, to phosgene.

See Oxidisable materials; below

Other reactants

Yoshida, 1980, 84

MRH values calculated for 14 combinations with oxidisable materials are given.

Oxidisable materials MRH Magnesium 6.02/25

1. Castrantas, 1965, 4
2. Sorbe, 1968, 43

Grinding the peroxide with oxidisable materials may cause fire [1], and the octahydrated solid explodes at high temperature [2].

Polysulfide polymers

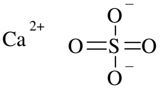
491M, 1975, 87

The dry peroxide, added to cause cross-linking in liquid polysulfide polymers with pendant thiol groups, caused sparking or ignition, depending on the scale of the process.

See other METAL PEROXIDES, OXIDANTS

3933. Calcium sulfate

[7778-18-9] **CaO_4S**



Aluminium

See Aluminium: Metal oxides, or Oxosalts

Diazomethane

See Diazomethane: Calcium sulfate

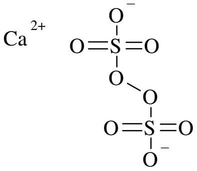
Phosphorus

See Phosphorus: Metal sulfates

See other METAL OXONON-METALLATES

3934. Calcium peroxodisulfate

[13235-16-0] **CaO_8S_2**



Castrantas, 1965, 6

It is shock-sensitive and explodes violently.

See other OXIDANTS, PEROXOACID SALTS

3935. Calcium sulfide

[20548-54-3] **CaS**

$$Ca{=}S$$

HCS 1980, 274

Oxidants

Mellor, 1941, Vol. 3, 745

Alkaline-earth sulfides react vigorously with chromyl chloride, lead dioxide, potassium chlorate (explodes lightly) and potassium nitrate (explodes violently).

See other METAL SULFIDES

3936. Calcium polysulfide

[1332-67-8] (tetrasulfide) [1332-68-9] (pentasulfide) **CaS_x**

$$Ca^{2+} \quad S^{-}{-}S^{-}$$

Edwards, P. W., *Chem. Met. Eng.*, 1922, **27**, 986

The powdered sulfide, admixed with small amounts of calcium thiosulfate and sulfur, has been involved in several fires and explosions, some involving initiation by static discharges.

See other METAL SULFIDES, STATIC INITIATION INCIDENTS

3937. Calcium silicide

[12013-55-7] **$CaSi$**

$$Ca^{2+} \quad Si^{2-}{=}Si^{2-} \quad Ca^{2+}$$

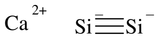
1. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
2. Yan, J. *et al., Chem. Abs.*, 1987, **107**, 182628
3. Deng. X. *et al., Arch. Combust.*, 1987, **7**(1—2), 19—31

The finely powdered silicide is a significant dust explosion hazard [1]. The lower explosion limit for a calcium—silicon dust cloud of mean particle size 9.7 μm was measured as 79 g/m3, in good agreement with a calculated value [2]. Other dust cloud parameters are presented and related to predictions [3].

Acids
Mellor, 1940, Vol. 6, 177
Interaction is vigorous, and the evolved silanes ignite in air.

Boron
See Boron: Calcium—silicon alloy
See other METAL NON-METALLIDES, PYROPHORIC MATERIALS

3938. Calcium disilicide
[12013-56-8] **$CaSi_2$**



Carbon tetrachloride
Zirconium Fire and Explosion Incidents, TID-5365, Washington, USAEC, 1956
Calcium disilicide exploded when milled in the solvent.

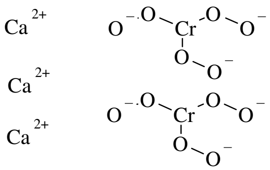
Iron(III) oxide
See Iron(III) oxide: Calcium disilicide

Metal fluorides
Berger, E., *Compt. rend.*, 1920, **170**, 29
Calcium disilicide ignites in close contact with alkali metal fluorides, forming silicon tetrafluoride.

Other reactants
Yoshida, 1980, 99
MRH values calculated for 14 combinations with oxidants are given.

Potassium nitrate
See Potassium nitrate: Calcium silicide
See other METAL NON-METALLIDES

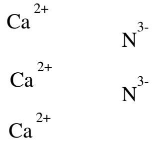
3939. Calcium triperoxochromate
[ ] **$Ca_3Cr_2O_{12}$**



Raynolds, J. A. *et al., J. Amer. Chem. Soc.*, 1930, **52**, 1851
A buff solid, prepared by means appropriate to a tetraperoxochromate(3-), it analysed as the dodecahydrate of this structure. It explodes at 100°C.
See other OXIDANTS, PEROXOACID SALTS

3940. Calcium nitride

[12013-82-0] **Ca_3N_2**



von Schwartz, 1918, 322

Spontaneously flammable in air (probably when finely divided and in moist air).

Halogens

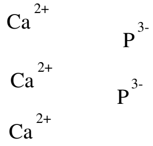
Mellor, 1940, Vol. 8, 103

Reaction with incandescence in chlorine gas or bromine vapour.

See other N-METAL DERIVATIVES, NITRIDES

3941. Calcium phosphide

[1305-99-3] **Ca_3P_2**



Dichlorine oxide

See Dichlorine oxide: Oxidisable materials

Oxygen

Van Wazer, 1958, Vol. 1, 145

Calcium and other alkaline-earth phosphides incandesce in oxygen at about 300°C.

Water

Mellor, 1940, Vol. 8, 841

Calcium and other phosphides on contact with water liberate phosphine, which usualy ignites in air, owing to the diphosphane content.

See other METAL NON-METALLIDES

3942. Columbium

[7440-03-1] **Cb**

Cb

See Niobium

3943. Cadmium

[7440-43-9] **Cd**

Cd

NSC 312, 1978; *HCS 1980*, 257; *RSC Lab. Hazards Safety Data Sheet No. 55*, 1987 (element and compounds)

The finely divided metal is pyrophoric.
See CADMIUM HYDRIDE
See other PYROPHORIC METALS

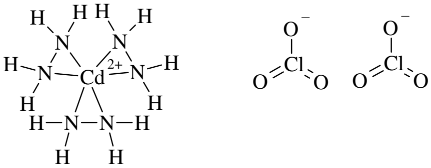
Hydrazoic acid
See Cadmium azide (reference 2)

Oxidants
See Nitryl fluoride: Metals
Ammonium nitrate: Metals

Selenium, or Tellurium
Mellor, 1940, Vol. 4, 480
Reaction on warming powdered cadmium with selenium or tellurium is exothermic, but less vigorous than that of zinc.
See other METALS

3944. Trihydrazinecadmium chlorate

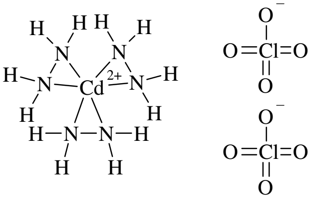
[ ] **$CdCl_2H_{12}N_6O_6$**



Mellor, 1956, Vol. 2, Suppl. 2.1, 592
It explodes on impact.
See other AMMINEMETAL OXOSALTS

3945. Basic trihydrazinecadmium perchlorate

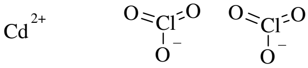
[ ] **$Cd_2Cl_2H_{14}N_6O_8$**



Mellor, 1967, Vol. 8, Suppl. 2, 88
The monohydrated basic salt is extremely explosive.
See related AMMINEMETAL OXOSALTS

3946. Cadmium chlorate

[10137-74-3] **$CdCl_2O_6$**



Sulfides

Mellor, 1956, Vol. 2, Suppl. 1, 584

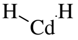
Interaction with copper(II) sulfide is explosive, and with antimony(II) sulfide, arsenic(III) sulfide, tin(II) sulfide and tin(IV) sulfide, incandescent.

See also Chloric acid: Metal sulfides

See other METAL CHLORATES, METAL CHLORATES: Phosphorus, etc., METAL OXOHALOGENATES

3947. Cadmium hydride

[72172-64-6] **CdH_2**



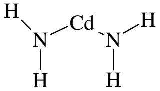
Barbaras, G. D. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 4585

The hydride, prepared at —78°C, suddenly decomposes during slow warming at 2°C, leaving a residue of pyrophoric cadmium.

See other METAL HYDRIDES

3948. Cadmium amide

[22750-53-4] **CdH_4N_2**



Alone, or Water

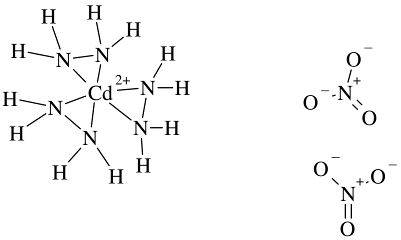
Mellor, 1940, Vol. 8, 261

When heated rapidly, the amide may explode. Reaction with water is violent.

See other N-METAL DERIVATIVES

3949. Trihydrazinecadmium(II) nitrate

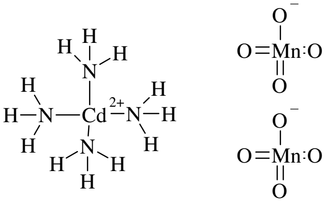
[82434-37-5] **$CdH_{12}N_8O_6$**



See HYDRAZINE METAL NITRATES

3950. Tetraamminecadmium permanganate

[34410-88-3] **$CdH_{12}Mn_2N_4O_8$**



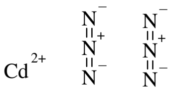
Mellor, 1942, Vol, 12, 335

It explodes on impact.

See other AMMINEMETAL OXOSALTS

3951. Cadmium azide

[14215-29-3] **CdN_6**



1. Turney, T. A., *Chem. & Ind.*, 1965, 1295
2. Mellor, 1967, Vol. 8, Suppl. 2.2, 25, 50
3. Schechkov, G. T., *Chem. Abs.*, 1983, **98**, 146010

A solution, prepared by mixing saturated solutions of cadmium sulfate and sodium azide in a 10 ml glass tube, exploded violently several hours after preparation [1]. The dry solid is extremely hazardous, exploding on heating or light friction. A violent explosion occurred with cadmium rods in contact with aqueous hydrogen azide [2]. A DTA study showed a l thermal stability than lead azide [3]. It is strongly endothermic (ΔH_f° (s) 451 kJ/mol, 2.32 kJ/g).

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

3952. Cadmium oxide

[1306-19-0] **CdO**

$Cd{=}O$

HCS 1980, 260

Magnesium

See Magnesium: Metal oxides

See other METAL OXIDES

3953. Cadmium selenide

[1306-24-7] **CdSe**

$Cd{\equiv}Se$

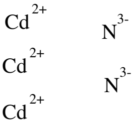
Preparative hazard

See Selenium: Metals

See related METAL SULFIDES

3954. Cadmium nitride

[12380-95-9] **Cd_3N_2**



$Cd^{2+}\ Cd^{2+}\ Cd^{2+}\ N^{3-}\ N^{3-}$

Fischer, F. *et al., Ber.*, 1910, **43**, 1469

The shock of the violent explosion caused by heating a sample of the nitride caused an unheated adjacent sample to explode. It is much less endothermic ($\Delta H°_f$(s) +161.5 kJ/mol, 0.44 kJ/g) than the azide.

Acids, or Bases

Mellor, 1964, Vol. 8, Suppl. 2.1, 161

It reacts explosively with dilute acids or bases.

Water

Mellor, 1940, Vol. 8, 261

It explodes on contact.

See other ENDOTHERMIC COMPOUNDS, N-METAL DERIVATIVES, NITRIDES

3955. Cerium

[7440-45-1] **Ce**

Ce

Alone, or Metals

Mellor, 1945, Vol. 5, 602—603

Cerium or its alloys readily give incendive sparks (pyrophoric particles) on frictional contact, this effect of iron alloys being widely used in various forms of ‘flint’ lighters. The massive metal ignites and burns brightly at 160°C, and cerium wire burns in a Bunsen flame more brightly than magnesium. Of its alloys with aluminium, antimony, arsenic, bismuth, cadmium, calcium, copper, magnesium, mercury, sodium and zinc, those containing major proportions of cerium are often extremely pyrophoric. The mercury amalgams ignite spontaneously in air without the necessity for frictional generation of small particles. The interaction of cerium with zinc is explosively violent, and with antimony or bismuth, very exothermic.

See other PYROPHORIC ALLOYS

Carbon dioxide, Nitrogen

See Carbon dioxide: Metals, Nitrogen

Halogens

Mellor, 1946, Vol. 5, 603

Cerium filings ignite in chlorine or in bromine vapour at about 215°C.

Phosphorus

See Phosphorus: Metals

Silicon

Mellor, 1946, Vol. 5, 605

Interaction at 1400°C to form cerium silicide is violently exothermic, often destroying the containing vessel.

Water

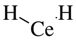
Uno, T. *et al., Anzen Kagaku*, 1988, **27**(3), 157—161 (*Chem. Abs.*, 1989, **110**, 12857)

The mixed alloy of cerium with lanthanum and other rare-earth metals (‘Mischmetall’) may ignite spontaneously in contact with aqueous solutions, owing to its oxidation by water and ignition of evolved hydrogen.

See other GAS EVOLUTION INCIDENTS, METALS, PYROPHORIC METALS, REDOX REACTIONS

3956. Cerium dihydride

[13569-50-1] **CeH_2**



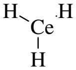
Libowitz, G. G. *et al., Inorg. Synth.*, 1973, **14**, 189—192

The polycrystalline hydride is frequently pyrophoric, particularly at higher hydrogen contents (up to $H_{2.85}$), while monocrystalline material appears to be less reactive to air.

See other METAL HYDRIDES

3957. Cerium trihydride

[13864-02-3] **CeH_3**



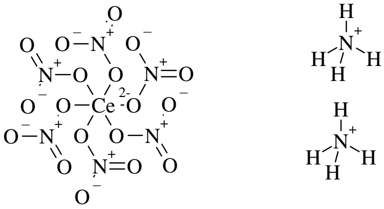
Muthmann, W. *et al., Ann.*, 1902, **325**, 261

The hydride is stable in dry air, but may ignite in moist air.

See other METAL HYDRIDES

3958. Ammonium hexanitrocerate (Ceric ammonium nitrate) (Ammonium cerium(IV) nitrate)

[16774-21-3] **$CeH_8N_8O_{12}$**



Cyclopentadienylsodium

See Sodium nitrate: Tris(cyclopentadienyl)sodium

Potassium bromate, Malonic acid, Water

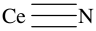
See Potassium bromate: Ceric ammonium nitrate, Malonic acid, Water.

See other OXIDANTS

See related METAL NITRATES

3959. Cerium nitride

[25764-08-3] **CeN**



Water

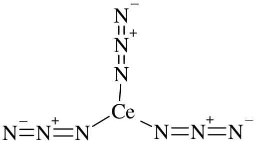
Mellor, 1940, Vol. 8, 121

Contact with water vapour slowly causes incandescence, while a limited amount of water or dilute acid causes rapid incandescence with ignition of evolved ammonia and hydrogen.

See other N-METAL DERIVATIVES, NITRIDES

3960. Cerium azide

[ ] **CeN_9**

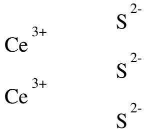


Mellor, 1940, Vol. 8, 354

The precipitate from cerium nitrate and sodium azide is explosive.

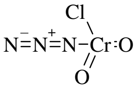
See other METAL AZIDES

3961. Cerium trisulfide
[12014-93-6] **Ce_2S_3**



Mellor, 1946, Vol. 5, 649
It is pyrophoric in ambient air when finely divided.
See other METAL SULFIDES, PYROPHORIC MATERIALS

3962. Chromyl azide chloride
[14259-67-7] **$ClCrN_3O_2$**

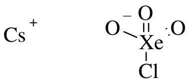


An explosive solid.
See entry METAL AZIDE HALIDES

3963. Caesium tetrafluorochlorate(1—)
[15321-04-7] **$ClCsF_4$**

Highly reactive oxidant.
See entry METAL POLYHALOHALOGENATES

3964. Caesium chloroxenate
[26283-13-6] **$ClCsO_3Xe$**



Jaselskis, B. *et al., J. Amer. Chem. Soc.*, 1967, **89**, 2770
It explodes at 205°C under vacuum.
See other XENON COMPOUNDS

3965. Chlorine fluoride
[7790-89-8] **ClF**

$Cl—F$

1. Sidgwick, 1950, 1149
2. ‘Product Information Sheet ClF’, Tulsa, Ozark-Mahoning Co., 1970

This powerful oxidant reacts with other materials similarly to chlorine trifluoride or fluorine [1], but more readily than the latter [2].

See Chlorine trifluoride, or Fluorine

Acetonitrile, Fluorine

See Fluorine: Acetonitrile, etc.

Aluminium

Mellor, 1956, Vol. 2, Suppl. 1, 63

Aluminium burns more readily in chlorine fluoride than in fluorine.

Bis (trifluoromethyl) sulfide

See Bis(trifluoromethyl) sulfide: Chlorine fluorides

Bis(trifluoromethyl) disulfide

See Bis(trifluoromethyl) disulfide: Chlorine fluorides

tert-Butanol

Young, D. F. *et al., J. Amer. Chem. Soc.*, 1970, **92**, 2314

A mixture prepared at —196°C exploded at —100°C during slow warming.

N-Chlorosulfinylamine

Kuta, G. S. *et al., Intern. J. Sulfur Chem.*, 1973, **8**, 335—340

Interaction of the reagents in equimolar proportions produced a highly explosive and strongly oxidising material (possibly an N—F compound).

Diethyl sulfite

See Ethyl fluorosulfate

Fluorocarbon polymers

‘Product Information Sheet ClF’, Tulsa, Ozark-Mahoning Co., 1970

Chlorine fluoride can probably ignite Teflon and Kel-F at high temperatures, or under friction or flow conditions.

Phosphorus trifluoride

1. Fox, W. B. *et al., Inorg. Nucl. Chem. Lett.*, 1971, **7**, 861
2. Neilson, R. H. *et al., Inorg. Chem.*, 1975, **14**, 2019

Interaction of the fluorides to produce chlorotetrafluorophosphorane [1] is uncontrollably violent even at —196°C [2]. An improved method of making the phosphorane from phosphorus pentafluoride and boron trichloride is detailed [2].

Tellurium

Mellor, 1943, Vol. 11, 26

Interaction is incandescent.

Trifluoromethanssulfenyl chloride

See Trifluoromethanesulfenyl chloride: Chlorine fluorides

Trifluorosulfur nitride

See *N,N*-Dichloropentafluorosulfanylamine

Trifluorosulfur nitride

Waterfeld, A. *et al., Angew. Chem. (Intern. Ed.)*, 1981, **20**, 1017

In the preparation of chloriminosulfur tetrafluoride or its dimer by slowly warming a mixture at —196° to —78°C and then ambient temperature, too rapid warming leads to violent explosions.

Water

Pascal, 1960, Vol. 16.1, 189

Interaction with liquid water or that bound in crystalline hydrates is violent.

See other INTERHALOGENS

3966. Fluoronium perchlorate

[ ] **$ClFH_2O_4$**

Water

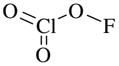
Hantzsch, A., *Ber.*, 1930, **63**, 97

This hydrogen fluoride—perchloric acid complex reacts explosively with water.

See other NON-METAL PERCHLORATES

3967. Chloryl hypofluorite

[101672-08-6] **$ClFO_3$**



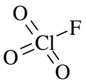
1. Hoffman, C. J., *Chem. Rev.*, 1964, **64**, 97
2. Christe, K. O. *et al., Inorg. Chem.*, 1987, **56**, 920

Not then completely purified or characterised, its explosive nature was in contrast to the stability of the isomeric perchloryl fluoride [1]. It is also shock-sensitive [2].

See other HALOGEN OXIDES, HYPOHALITES

3968. Perchloryl fluoride

[7616-94-6] **$ClFO_3$**



1. ‘Booklet DC-1819’, Philadelphia, Pennsalt Chem. Corp., 1957
2. Anon., *Chem. Eng. News*, 1960, **38**, 62
3. Barton, D. H. R., *Pure Appl. Chem.*, 1970, **21**, 185
4. Sharts, C. M. *et al., Org. React.*, 1974, **21**, 232—234

Procedures relevant to safe handling and use are discussed. Perchloryl fluoride is stable to heat, shock and moisture, but is a powerful oxidiser comparable with liquid oxygen. It forms flammable and/or explosive mixtures with combustible gases and vapours [1,2]. It only reacts with strongly nucleophilic centres, and the by-product, chloric acid is dangerously explosive in admixture with organic compounds [3]. Safety aspects of practical use of perchloryl fluoride have been reviewed [4].

Benzocyclobutene, Butyllithium, Potassium *tert*-butoxide

Adcock, W. *et al., J. Organomet. Chem.*, 1975, **91**, C20

An attempt to convert benzocyclobutenylpotassium (prepared from the reagents above) to the fluoro derivative at —70°C with excess perchloryl fluoride led to a violent explosion when the reaction mixture was removed from the cooling bath after stirring for an hour.

Calcium acetylide, or Potassium cyanide, or Potassium thiocyanate, or Sodium iodide

Kirk-Othmer, 1966, Vol. 9, 602

Unreactive at 25°, these solids react explosively in the gas at 100—300°C.

Charcoal

Inman, C. E. *et al., Friedel-Craft and Related Reactions*, (Olah, G. A., Ed.), Vol. 3, 1508, New York, Interscience, 1964

Adsorption of perchloryl fluoride on charcoal can, like liquid oxygen, produce a powerful ‘Sprengel’ explosive.

Ethyl 4-fluorobenzoylacetate

Fuqua, S. A. *et al., J. Org. Chem.*, 1964, **29**, 395, footnote 3

Fluorination of the ester with perchloryl fluoride by an established method led to a violent explosion.

Finely divided solids

McCoy, G., *Chem. Eng. News*, 1960, **38**(4), 62

Oxidisable organic materials of high surface to volume ratio (carbon powder, foamed elastomers, lampblack, sawdust) react very violently, even at —78°C, with perchloryl fluoride, which should be handled with the same precautions as liquid oxygen.

Hydrocarbons, or Hydrogen sulfide, or Nitrogen oxide, or Sulfur dichloride, or Vinylidene chloride

Braker, 1980, 578

At ambient temperature, perchloryl fluoride is unreactive with the compounds above, but reaction is explosive at 100—300°C, or if the mixtures are ignited.

3α-Hydroxy-5β-androstane-11,17-dione 17-hydrazone

Nomine, G. *et al., J. Chem. Educ.*, 1969, **46**, 329

A reaction mixture in aqueous methanol exploded violently at —65°C. (Hydrazine—perchloryl fluoride redox reaction?) A previous reaction at 20°C had been uneventful, and the low-temperature explosion could not be reproduced.

Laboratory materials

Schlosser, M. *et al., Chem. Ber.*, 1969, **102**, 1944

Contact of perchloryl fluoride with laboratory greases or rubber tubing, etc., has led to several explosions.

Lithiated compounds

Houben-Weyl, 1970, Vol. 13.1, 223

There is a danger of explosion during replacement of a lithium substituent by fluorine using perchloryl fluoride.

See Benzocyclobutene, etc., above

2-Lithio(dimethylaminomethyl)ferrocene

Peet, J. H. J. *et al., J. Organomet. Chem.*, 1974, **82**, C57

Preparation of dimethylaminomethyl-2-fluoroferrocene, by interaction of the lithio compound in THF at —70°C with perchloryl fluoride diluted with helium, unexpectedly exploded violently.

Methyl 2-bromo-5,5-(ethylenedioxy)[2.2.1]bicycloheptane-7-carboxylate

Wang, C.-L. J. *et al., J. Chem. Soc., Chem. Comm.*, 1976, 468

In an attempt to improve isomer distribution from the fluorination reaction, one run was cooled to below —40°C, but on quenching with water, a violent explosion occurred.

Nitrogenous bases

1. Scott, F. L. *et al., Chem. & Ind.*, 1960, 258
2. Gardner, D. M. *et al., J. Org. Chem.*, 1967, **32**, 1115
3. Parish, E. J. *et al., J. Org. Chem.*, 1980, **45**, 4036—4037

Interaction, in presence of diluent below 0°C, with isopropylamine or isobutylamine caused separation of explosive liquids, and with aniline, phenylhydrazine and 1,2-diphenylhydrazine, explosive solids [1]. In absence of diluents, contact with most aliphatic or non-aromatic heterocyclic amines often leads to uncontrolled oxidation and/or explosions [2]. During oxidation of two steroidal dienes in dry pyridine at —35 to —40°C, on one occasion each of the reactions was accompanied by violent explosions [3].

See 3α-Hydroxy-5β-androstane-11,17-dione 17-hydrazone, above

Podophyllotoxin enolate tetrahydropyranyl ether

Glinski, M. B. *et al., J. Org. Chem.*, 1987, **53**, 2749—2753

Attempted preparation of 2-fluoropodophyllotoxin by treatment of the tetrahydropyranyl ether with perchloryl fluoride led to a violent explosion.

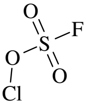
Sodium methoxide, Methanol

Papesch, V., *Chem. Eng. News*, 1959, **36**, 60

Addition of solid methoxide to a reaction vessel containing methanol vapour and gaseous perchloryl fluoride caused ignition and explosion. This could be avoided by adding all the methoxide first, or by nitrogen purging before addition of methoxide.

See other HALOGEN OXIDES, PERCHLORYL COMPOUNDS

3969. Chlorine fluorosulfate
[13997-90-5] **$ClFO_3S$**

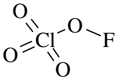


Bailar, 1973, Vol. 2, 1469

Hydrolysis is violent, producing oxygen.

See related ACYL HALIDES, HYPOHALITES

3970. Fluorine perchlorate (Perchloryl hypofluorite)
[10049-03-3] **$ClFO_4$**



Alone, or Laboratory materials, or Potassium iodide

1. Rohrback, G. H. *et al., J. Amer. Chem. Soc.*, 1949, **69**, 677
2. Christe, K. O. *et al., Inorg. Chem.*, 1982, **21**, 2938

The pure liquid explodes on freezing at —167°C, and the gas is readily initiated by sparks, flame or contact with grease, dust or rubber tubing. Contact of the gas with aqueous potassium iodide also caused an explosion [1]. The pure material is now readily accessible via the relatively stable intermediate, tetrafluoroammonium perchlorate [2].

Bis(trifluoromethanesulfonyl)imide

See N-Chlorobis(trifluoromethanesulfonyl)imide

Difluorimide—potassium fluoride adduct

Christe, K. O. *et al., Inorg. Chem.*, 1987, 56, 925

A mixture prepared at —196°C exploded when warmed towards —78°C.

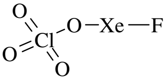
Hydrogen

Hoffman, C. J., *Chem. Rev.*, 1964, **64**, 97

Ignition of the perchlorate occurs in excess hydrogen gas.

See other HALOGEN OXIDES, HYPOHALITES

3971. Xenon(II) fluoride perchlorate
[25582-86-9] **$ClFO_4Xe$**



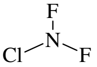
Bartlett, N. *et al., Chem. Comm.*, 1969, 703

Thermodynamically unstable, it explodes readily and sometimes with violence.

See other NON-METAL PERCHLORATES, XENON COMPOUNDS

3972. Nitrogen chloride difluoride

[13637-87-1] **ClF_2N**



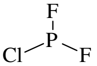
Petry, R. C., *J. Amer. Chem. Soc.*, 1960, **82**, 2401

Caution in handling is recommended for this *N*-halogen compound.

See other N-HALOGEN COMPOUNDS

3973. Phosphorus chloride difluoride

[14335-40-1] **ClF_2P**



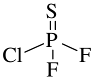
Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

See other NON-METAL HALIDES

3974. Thiophosphoryl chloride difluoride

[2524-02-9] **ClF_2PS**



Mellor, 1971, Vol. 8, Suppl. 3, 536

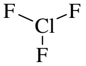
Mixtures with air explode spontaneously at certain concentrations.

See other AUTOIGNITION INCIDENTS

See related NON-METAL HALIDES (AND THEIR OXIDES)

3975. Chlorine trifluoride

[7790-91-2] **ClF_3**



1. Anon., *J. Chem. Educ.*, 1967, **44**, A1057—1062
2. O'Connor, D. J. *et al., Chem. & Ind.*, 1957, 1155
3. Farrar, R. L. *et al., Some Considerations in Handling Fluorine and Chlorine Fluorides*, Oak Ridge Rept. K/ET-252, 1979, 41pp

Handling procedures for this highly reactive oxidant gas have been detailed [1]. Surplus gas is best burned with town- or natural gas, followed by absorption in alkali [2]. More recent and comprehensive information is available [3].

Acids MRH Sulfuric acid 1.17/34

Mellor, 1956, Vol. 2, Suppl. 1, 157

Strong nitric and sulfuric acids reacted violently, (possibly owing to water content).

Ammonium fluoride, or Ammonium hydrogen fluoride

Gardner, D. M. *et al., Inorg. Chem.*, 1963, **2**, 413

The reaction gases (containing chlorodifluoramine) must be handled at below —5°C to avoid explosion. Ammonium hydrogen fluoride behaves similarly.

Bis(trifluoromethyl) sulfide, or disulfide

See Bis(trifluoromethyl) sulfide: Chlorine fluorides
Bis(trifluoromethyl) disulfide: Chlorine fluorides

Boron-containing materials

Bryant, J. T. *et al., J. Spacecr. Rockets*, 1971, **8**, 192—193

Finely divided boron, tetraboron carbide, and boron—aluminium mixtures will ignite on exposure to the gas.

See Metals, etc., below

Carbon tetrachloride MRH 1.21/56

Mellor, Vol. 2, Suppl. 1, 156

Chlorine trifluoride will dissolve in carbon tetrachloride at low temperatures without reaction. Such solutions are dangerous, being capable of detonation. If it is used as a solvent for fluorination with the trifluoride, it is therefore important to prevent build-up of high concentrations of the latter.

Chromium trioxide

Mellor, 1943, Vol. 11, 181

Interaction of the two oxidants is incandescent.

Deuterium, or Hydrogen MRH Hydrogen 6.82/3.0

Haberland, H. *et al., Chem. Phys.*, 1975, **10**, 36

Studies of the interaction of chlorine trifluoride with deuterium or hydrogen atoms in a scattering chamber were accompanied by frequent flashes or explosions, within 3 h if the reactor had been vented, or after 8 h if it had not.

Fluorinated solvents

'Chlorine Trifluoride', Tech. Bull. TA 8522-3, Morristown, N.J., Baker & Adamson Div. of Allied Chemicals Corp., 1968

Bulk surfaces of polytetrafluoroethylene or polychlorotrifluoroethylene are resistant to the liquid or vapour under static conditions, but breakdown and ignition may occur under flow conditions.

See Polychlorotrifluoroethylene, below

Fuels

See ROCKET PROPELLANTS

Halocarbons

Brower, K. R., *J. Fluorine Chem.*, 1986, **31**, 333—349

Combinations of liquid chlorine trifluoride with several halocarbons except perfluorohexane exploded immediately when suddenly mixed at all temperatures between 25° and —70°C.

See Carbon tetrachloride, Fluorinated solvents, both above
Poly(chlorotrifluoroethylene), below

Hydrocarbons
Brower, K. R., *J. Fluorine Chem.*, 1986, **31**, 333—349
Combinations of liquid chlorine trifluoride and several hydrocarbons exploded immediately when suddenly mixed at all temperatures between 25° and —70°C.
See Organic materials, below

Hydrogen sulfide 4.68/13
Mellor, 1956, Vol. 2, Suppl. 1, 157
Explosive reactions occur with ammonia, coal-gas, hydrogen or hydrogen sulfide.

Hydrogen-containing materials MRH Ammonia 5.52/16,

Ice
See Water, below

Iodine
Mellor, 1956, Vol. 2, Suppl. 1, 157
Ignition on contact.

Metals, or Metal oxides, or Metal salts, or Non-metals, or Non-metal oxides MRH Iron 5.10/68, potassium 2.90/63, Calcium oxide 4.05/48, magnesium oxide 3.89/39, manganese dioxide 1.80/48, Calcium oxide 4.05/48, magnesium oxide 3.89/39, manganese dioxide 1.80/48, Sulfur 4.10/15, silver nitrate 0.5/73

1. Mellor, 1956, Vol. 2, Suppl. 1, 155—157
2. Sidgwick, 1950, 1156
3. Rhein, R. A., *J. Spacecr. Rockets*, 1969, **6**, 1328—1329
4. ‘Chlorine Trifluoride’ Tech. Bull. TA 8532-3, Morristown, N. J., Baker & Adamson Div. Allied Chem. Corp., 1968

Chlorine trifluoride is a hypergolic oxidiser with recognised fuels, and contact with the materials following at ambient or slightly elevated temperatures is violent, ignition often occurring. The state of subdivision may affect the results.

Antimony, arsenic, selenium, tellurium, iridium, iron, molybdenum, osmium, potassium, rhodium, tungsten; (and when primed with charcoal,) aluminium, copper, lead, magnesium, silver, tin, zinc. Interaction of lithium or calcium with chlorine tri- or penta-fluorides is hypergolic and particularly energetic.

Aluminium oxide, arsenic trioxide, bismuth trioxide, calcium oxide, chromic oxide, lanthanum oxide, lead dioxide, magnesium oxide, manganese dioxide, molybdenum trioxide, phosphorus pentoxide, stannic oxide, sulfur dioxide (explodes), tantalum pentoxide, tungsten trioxide, vanadium pentoxide.

Red phosphorus, sulfur; but with carbon, the observed ignition has been attributed to presence of impurities; mercury iodide, potassium iodide, silver nitrate, potassium carbonate.

Methane

Baddiel, C. B. *et al., Proc. 8th Combust. Symp.*, 1960, 1089—1095

The explosive interaction of chlorine trifluoride with methane and its homologues has been studied in detail.

Nitroaryl compounds

Mellor, 1956, Vol. 2, Suppl. 1, 156

Several nitro compounds are soluble in chlorine trifluoride, but the solutions are extremely shock-sensitive. These include trinitrotoluene, hexanitrobiphenyl, hexanitrodiphenyl-amine, -sulfide or -ether. Highly chlorinated compounds behave similarly.

Organic materials MRH Acetic acid 3.05/19, benzene 5.35/36, ether 5.56/28

Mellor, 1956, Vol. 2, Suppl. 1, 155

Violence of the reaction, sometimes explosive, with e.g., acetic acid, benzene, ether, is associated with both their carbon and hydrogen contents. If nitrogen is also present, explosive fluoroamino compounds may be involved. Fibrous materials —cotton, paper, wood — invariably ignite.

Other reactants

Yoshida, 1980, 129

MRH values calculated for 18 combinations with oxidisable materials are given.

Polychlorotrifluoroethylene

Anon., *Chem. Eng. News*, 1965, **43**(20), 41

An explosion occurred when chlorine trifluoride was being bubbled through the fluorocarbon oil at —4°C. Moisture (snow) may have fallen into the mixture, reacted exothermally with the trifluoride and initiated the mixture.

See Water, below

Refractory materials

1. Cloyd, 1965, 58
2. Mellor, 1956, Vol. 2, Suppl. 1, 157

Fibrous or finely divided refractory materials, asbestos, glass wool, sand, or tungsten carbide, may ignite with the liquid and continue to burn in the gas [1]. The presence of adsorbed or lattice water seems necessary for attack on the siliceous materials to occur [2].

See other GLASS INCIDENTS

Ruthenium

Burns. R. C. *et al., J. Inorg. Nucl. Chem.*, 1980, **42**, 1614

Formation of the adduct chlorine trifluoride—ruthenium pentafluoride by reaction with ruthenium metal at ambient temperature is extremely violent.

Selenium tetrafluoride

See Selenium tetrafluoride: Chlorine trifluoride

Trifluoromethanesulfenyl chloride

See Trifluoromethanesulfenyl chloride: Chlorine fluorides

Water

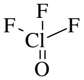
1. Sidgwick, 1950, 1156
2. Mellor, 1956, Vol. 2, Suppl. 1, 156, 158
3. Ruff, O. *et al., Z. Anorg. Chem.*, 1930, **190**, 270
4. Farrar, R. L. *et al.*, USDOE Rept. K/ET-252, 1979, 41

Interaction is violent and may be explosive, even with ice, oxygen being evolved [1]. Part of the water dropped into a flask of the gas was expelled by the violent reaction ensuing [2]. An analytical procedure, involving absorption of chlorine trifluoride into 10% sodium hydroxide solution from the open capillary neck of a quartz ampoule to avoid explosion, was described [3]. Inadvertent collection of chlorine trifluoride and ice in a cryogenic trap led to a small but violent explosion when the trap began to warm up overnight [4].

See other INTERHALOGENS

3976. Chlorine trifluoride oxide

[30708-80-6] **ClF_3O**



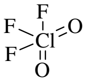
Bougon, R. *et al.*, Fr. Pat. 2 110 555, 1972

It is a powerful oxidant, potentially useful in rocketry.

See other HALOGEN OXIDES

3977. Chlorine dioxygen trifluoride

[12133-60-7] **ClF_3O_2**



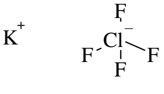
Organic materials

1. Streng, A. G., *Chem. Rev.*, 1963, **63**, 607
2. Christe, K. O. *et al., Inorg. Chem.*, 1973, **12**, 1357

It is a very powerful oxidant, but of low stability, which reacts explosively with organic materials [1]; such combinations should be avoided [2].

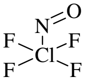
3978. Potassium tetrafluorochlorate(1—)

[19195-69-8] **ClF_4K**



See entry METAL POLYHALOHALOGENATES

3979. Nitrosyl tetrafluorochlorate
[13815-21-9] **ClF_4NO**



Organic compounds

Sorbe, 1968, 133

The powerful oxidant reacts explosively with many organic compounds.

See other NITROSO COMPOUNDS, OXIDANTS

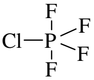
3980. Tetrafluoroammonium perchlorate
[13706-14-4] **ClF_4NO_4**

Christe, K. O. *et al., Inorg. Chem.*, 1980, **19**, 1495

It decomposes rapidly at 25°C, giving the very shock-sensitive chloryl hypofluorite.

See other N-HALOGEN COMPOUNDS, PERCHLORATE SALTS OF NITROGENOUS BASES

3981. Chlorotetrafluorophosphorane
[13637-88-2] **ClF_4P**

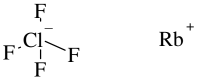


Preparative hazard

See Chlorine fluoride: Phosphorus trifluoride

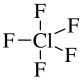
See other NON-METAL HALIDES

3982. Rubidium tetrafluorochlorate(1—)
[15321-10-5] **ClF_4Rb**



See entry METAL POLYHALOHALOGENATES

3983. Chlorine pentafluoride
[13637-63-3] **ClF_5**



Metals

See Chlorine trifluoride: Metals

Nitric acid

Christe, K. O., *Inorg. Chem.*, 1972, **11**, 1220

Interaction of anhydrous nitric acid with chlorine pentafluoride vapour at —40°C, or with the liquid at above —100°C, is very vigorous.

Water

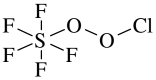
1. Pilipovich, D. *et al., Inorg. Chem.*, 1967, **6**, 1918
2. Christe, K. O., *Inorg Chem.*, 1972, **11**, 1220

Interaction of liquid chlorine pentafluoride with ice at —100°C [1], or of the vapour with water vapour above 0°C [2], is extremely vigorous.

See other INTERHALOGENS

3984. Pentafluorosulfur peroxyhypochlorite

[58249-49-3] **ClF_5O_2S**



Haloalkenes

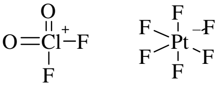
Hopkinson, M. J. *et al., J. Org. Chem.*, 1976, **41**, 1408

The peroxyhypochlorite is especially reactive, and the fluoroperoxy compounds produced by its interaction with haloalkenes can detonate when subjected to thermal or mechanical shock. However, no explosions were experienced during this work.

See related FLUORINATED PEROXIDES AND SALTS, HYPOHALITES

3985. Difluoroperchloryl hexafluoroplatinate

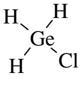
[36609-92-4] **ClF_8O_2Pt**



See entry DIFLUOROPERCHLORYL SALTS

3986. Chlorogermane

[13637-65-5] **$ClGeH_3$**



Ammonia

Johnson, O. H., *Chem. Rev.*, 1951, **48**, 274

Both mono- and di-chlorogermanes react with ammonia to give involatile products (presumably with N—Ge bonds) which explode on heating.
See other AMINATION INCIDENTS
See related METAL HALIDES, METAL HYDRIDES

3987. Hydrogen chloride (Hydrochloric acid)

[7647-01-0] **ClH**

$H^+ \quad Cl^-$

FPA H41, 1975 (gas); *HCS 1980*, 546 (cylinder); *HCS 1980*, 541 (solution)

Alcohols, Hydrogen cyanide

1. Pinner, A., *Die Imidoäther*, Berlin, Openheim, 1892
2. Erickson, J. G., *J. Org. Chem.*, 1955, **20**, 1573

Preparation of alkyliminioformate chlorides (imidoester hydrochlorides) by passing hydrogen chloride rapidly into alcoholic hydrogen cyanide proceeds explosively (probably owing to a rapid exotherm), even with strong cooling [1]. Alternative procedures involving very slow addition of hydrogen chloride into a well-stirred mixture kept cooled to ambient temperature, or rapid addition of cold alcoholic hydrogen cyanide to cold alcoholic hydrogen chloride, are free of this hazard [2].

Aluminium MRH 3.05/20

See Aluminium: Hydrogen chloride
Aluminium—titanium alloys: Oxidants

Caesium telluroacylates

Kato, S. *et al., J. Amer. Chem. Soc.*, 1995, **116**(12), 1262

While generating tellurobenzoic acids by acidifying the corresponding cesium salts with hydrogen chloride in tubes immersed in liquid nitrogen, it was found that explosions sometimes occurred while later allowing the reaction tube to warm. This is due to overcooling; HCl freezes, and therefore becomes unreactive, well above liquid nitrogen temperature, permitting sudden and exothermic reaction during the warming period.

Chlorine, Dinitroanilines

1. Sihlbohm, L., *Acta Chem. Scand.*, 1953, **7**, 1197—1206
2. Harris, G. P. F. *et al., Chem. & Ind.*, 1983, 183

The previously reported cleavage of dinitroanilines to chloronitrodiazonium salts by hydrochloric acid [1] is apparently catalysed by chlorine or other oxidants. The reaction takes place vigorously with copious gas evolution, but at low temperatures (40—25°C or lower) there can be a very long induction period before onset of the vigorous reaction. This could be hazardous on attempting to scale-up laboratory processes. The reactivity of the isomeric dinitroanilines varies, 2,3- being most reactive and 3,5- being unreactive. The cleavage reaction is specific for conc. hydrochloric acid, and has not been observed with hydrobromic acid or 30% sulfuric acid [2].
See other GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS

1,1-Difluoroethylene
See 1,1-Difluoroethylene: Hydrogen chloride

Fluorine MRH 3.18/35
See Fluorine: Hydrogen halides

Hexalithium disilicide
See Hexalithium disilicide: Acids

Metal acetylides or carbides MRH Calcium carbide 3.97/46
See Caesium acetylide: Mineral acids
Rubidium acetylide: Acids
Uranium dicarbide: Hydrogen chloride

Metals
Anon., *Loss Prev. Bull.*, 1994, (116), 22
Hydrochloric acid is capable of evolving hydrogen on reaction with many common metals. A magnetic flow meter is reported as exploding after the acid reached the electric amplifier compartment.

Other reactants
Yoshida, 1980, 55
MRH values calculated for 11 combinations, largely with oxidants, are given.

Potassium permanganate MRH 0.75/37
See Potassium permanganate: Hydrochloric acid

Preparative hazard
See Sulfuric acid, below

Silicon dioxide
See Silicon dioxide: Hydrochloric acid

Sodium
See Sodium: Acids

Sulfuric acid.
1. *MCA Case History No. 1785*
2. Libman, D. D., *Chem. & Ind.*, 1948, 728
3. Smith, G. B. L. *et al., Inorg. Synth.*, 1950, **3**, 132

Accidental addition of 6500 l of conc. hydrochloric acid to a bulk sulfuric acid storage tank released sufficient hydrogen chloride gas by dehydration to cause the tank to burst violently [1]. Complete dehydration of hydrochloric acid solution releases some 250 volumes of gas. A laboratory apparatus for effecting this safely has been described [2], which avoids the possibility of layer formation in unstirred flask generators [3].
See other GAS EVOLUTION INCIDENTS

Tetraselenium tetranitride
See Tetraselenium tetranitride: Alone, or Halogens and derivatives
See other INORGANIC ACIDS, NON-METAL HALIDES, NON-METAL HYDRIDES

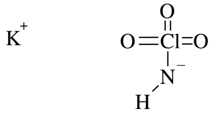
'Urea ammonium nitrate'

Internet, US Chem. Safety & Haz. Investigation Board, CSB 1999-4319

A delivery of the above was charged to a hydrochloric acid tank, poisonous yellow-green fumes were evolved.

3988. Monopotassium perchlorylamide

[16971-92-9] **$ClHKNO_3$**



Sorbe, 1968, 67

Like the dipotassium salt, it will explode on impact or exposure to flame.

See entry PERCHLORYLAMIDE SALTS

See other N-METAL DERIVATIVES

3989. Hypochlorous acid

[7790-92-3] **ClHO**

$H^+ \quad \overset{-}{O}{-}Cl$

Acetic anhydride

Rüst, 1948, 341

A mixture of the anhydride and hypochlorous acid exploded violently while being poured. Some acetyl hypochlorite and/or dichlorine monoxide may have been formed.

Alcohols

Mellor, 1956, Vol. 2, Suppl. 1, 560

Contact of these, or of chlorine and alcohols, readily forms unstable alkyl hypochlorites.

See other HYPOHALITES

Ammonia

Mellor, 1940, Vol. 8, 217

The violent explosion occurring on contact with ammonia gas is due to formation of nitrogen trichloride and its probable initiation by the heat of solution of ammonia.

See Chloramine (reference 3)

Arsenic

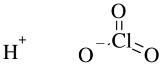
Mellor, 1941, Vol. 2, 254

Ignition occurs on contact.

See other HYPOHALITES, OXOHALOGEN ACIDS

3990. Chloric acid

[7790-93-4] **$ClHO_3$**



Muir, G. D., private comm., 1968
Aqueous chloric acid solutions decompose explosively if evaporative concentration is carried too far.

Cellulose
Mellor, 1946, Vol. 2, 310
Filter paper ignites after soaking in chloric acid.

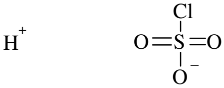
Metal sulfides
Mellor, 1956, Vol. 2, Suppl. 1, 584
Copper sulfide explodes with concentrated chloric acid solution (and also with cadmium, magnesium or zinc chlorates). Antimony trisulfide or arsenic trisulfide, or tin(II) and (IV) sulfides react incandescently with concentrated solutions.

Metals, or Organic materials
Majer, V., *Chemie* (Prague), 1948, **3**, 90—91
The recorded explosions of chloric acid have been attributed to the formation of explosive compounds with antimony, bismuth and iron (including hydrogen also in the latter case). Organic materials (and ammonia) are violently oxidised.

Oxidisable materials
In contact with oxidisable materials, reactions are similar to those of the metal chlorates.
See entry METAL CHLORATES
See other OXOHALOGEN ACIDS

3991. Chlorosulfuric acid

[7790-94-5] **$ClHO_3S$**



FPA H122, 1983; *HCS 1980*, 314

Diphenyl ether
Ehama, T. *et al.*, Jap. Pats. 74 45 034, 74 45 035, 1974
Presence of various nitrogen-containing compounds, or of fatty acids or their derivatives, controls the vigorous interaction of the ether and chlorosulfuric acid at above 40°C, producing higher yields of 4,4’-oxybisbenzenesulfonyl chloride.

Hydrocarbons MRH Hexane, 0.96/24; Toluene, 1.29/37
1. Anon., *CIHSC Chem. Safety Summ.*, 1986, **57**(226), 65

2. Baker J. D., *Chem. Eng. News*, 1989, **67**(50), 2

Use of heptane to wash sludge from a chlorosulfuric acid weigh tank led to violent rupture of the 2.5 kl vessel. Laboratory work showed that the two compounds react vigorously with gas evolution (HCl) sufficient to overpressure the tank which was fitted with a 40 mm relief line [1]. Another(?) tank containing chlorosulfonic acid ruptured after the lines to it were washed out with heptane, subsequent investigation showed that chlorosulfonic acid gives reaction, with large gas evolution, when stirred with commercial heptane fractions (and with hexane, but not cyclohexane, in the editor's experience.) Subsequent correspondence sought to attribute the observation to water contamination, which seems unlikely [2].

See other GAS EVOLUTION INCIDENTS, SULFONATION INCIDENTS

Other reactants

Yoshida, 1980, 115—116

MRH values calculated for 21 combinations, mainly with oxidisable materials, are given.

Phosphorus

Heumann, K. *et al., Ber.*, 1882, **15**, 417

The acid is a strong oxidant, and above 25—30°C, interaction is vigorous and accelerates to explosion.

Silver nitrate

See Silver nitrate: Chlorosulfuric acid

Sulfuric acid

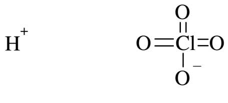
Anon., *Loss Prev. Bull.*, 1977, (013), 2—3

Failure to start an agitator before charging 500 kg of 98% sulfuric acid (d = 1.84) into 560 kg of chlorosulfuric acid (d = 1.44) led to formation of a lower layer of sulfuric acid. Subsequent starting of the agitator led to eruption of part of the contents owing to rapid formation of hydrogen chloride gas from interaction of the chlorosulfuric acid with the water content (2%) in the sulfuric acid.

See other ACYL HALIDES, GAS EVOLUTION INCIDENTS, INORGANIC ACIDS, OXIDANTS

3992. Perchloric acid

[7601-90-3] **$ClHO_4$**



(*MCA SD-11*, 1965); *NSC 311*, 1982; *FPA H53*, 1977; *HCS 1980*, 721

1. *MCA SD-11*, 1965
2. Lazerte, D., *Chem. Eng. News*, 1971, **49**(3), 33
3. Muse L. A., *J. Chem. Educ.*, 1972, **49**, A463
4. Graf, F. A., *Chem. Eng. Progr.*, 1966, **62**(10), 109
5. Friedmann, W., *Chem. Eng. News*, 1947, **25**, 3458

6. Anon., *ABCM Quart. Safety Summ.*, 1936, **7**, 51
7. Annikov, V. E. *et al., Chem. Abs.*, 1983, **99**, 160860
8. Anon., *Indian Chem. Manuf.*, 1976, **14**(5), 9—13
9. Schilt, A. A., *Perchloric Acid and Perchlorates*, Columbus (Oh.), G. F. Smith Chemical Co., 1979
10. Furr, A. K. (Ed.), *Handbook of Laboratory Safety*. 3rd Edn., 207, CRC Press, Boca Raton (Florida), 1990.

Most of the numerous and frequent hazards experienced with perchloric acid have been associated with either its exceptional oxidising power or the inherent instability of its covalent compounds, some of which form readily. Although the 70—72% acid of commerce behaves when cold as a very strong, but non-oxidising acid, it becomes an extreme oxidant and powerful dehydrator at elevated temperatures (160°C) or when anhydrous [1].

Where an equally strong but non-oxidising acid can be used, trifluoromethanesulfonic acid is recommended [2]. Safe handling procedures have been detailed [3] and an account of safe handling of perchloric acid in large-scale preparation of hydrazinium diperchlorate, with recommendations for materials of construction, has been published [4]. The lack of oxidising power of the unheated 72% aqueous acid was confirmed during analytical treatment of oil sludges on over 100 occasions [5]. A report of two explosions during evaporation of aqueous perchloric acid in a method for estimating potassium infers that the aqueous acid may be unstable. It is more likely that oxidisable material (probably ethanol) was present during the evaporation [6]. The aqueous acid can be caused to detonate with a booster charge [7]. Safety procedures for using perchloric acid for various purposes have been reviewed [8], and the section on safety aspects in a text [9] is rated by a reviewer as particularly pertinent. Precautions for using perchloric acid and perchlorates are given, and many incidents described in [10].

Acetic anhydride

See Dehydrating agents, below (references 2—4)

Acetic anhydride, Acetic acid, Organic materials

1. Burton, H. *et al., Analyst*, 1955, **80**, 4
2. Schumacher, 1960, 187, 193
3. Kuney, J. H., *Chem. Eng. News*, 1947, **25**, 1659
4. *Tech. Survey No. 2, Fire Hazards and Safeguards for Metalworking Industries*, US Board of Fire Underwriters, 1954
5. Editor's comment

Mixtures of 70% (dihydrated) perchloric acid with enough acetic anhydride will produce a solution of anhydrous perchloric acid in acetic acid/anhydride, which is of high catastrophic potential [1]. Sensitivity to heat and shock depend on the composition of the mixture, and the vapour evolved on heating is flammable [2]. Such solutions have been used for electropolishing operations, and during modifications to an electroplishing process by the unqualified supervisor, a cellulose acetate rack was introduced into a large volume of an uncooled mixture of perchloric acid and acetic anhydride. Dissolution of the rack introduced organic materials (largely cellulose acetate, capable of transesterification to cellulose perchlorate) into the virtually

anhydrous acid and caused the whole to explode disastrously, causing enormous damage. This cause was confirmed experimentally [3,4]. Mixtures are apparently used by metallurgists for sample preparation. Even those too dilute to be a direct explosion hazard will decompose, generating gas, on standing, especially after contact with catalytic metals. They should not be stored in sealed bottles [5].
See Acetic anhydride: Perchloric acid
See Alcohols; Cellulose and derivatives; Vegetable matter, all below

Acetic anhydride, Carbon tetrachloride, 2-Methylcyclohexanone
Gall, M. *et al., Org. Synth.*, 1972, **52**, 40
During acetylation of the enolised ketone, the 70% perchloric acid must be added last to the reaction mixture to provide maximum dilution and cooling effect.

Acetic anhydride, Organic materials, Transition metals
Hikita, T. *et al., J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1951, **54**, 253—255
The stability ranges of mixtures of the acid, anhydride and organic materials (ethanol, gelatine) used in electropolishing were studied. Presence of transition metals (chromium, iron, nickel) increases the possibility of explosion. (This is why such mixtures must not be stored after use for etching metals.)

Acetonitrile
Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542—545
The latent hazards in storing and handling the explosive mixtures of perchloric acid with acetonitrile or dimethyl ether are discussed.

Acetylene, Nitrous oxide
1. Hobson, J. D., *Chem. Brit.*, 1985, **21**, 632
2. Anon., *Lab. Haz. Bull.*, 1987, (9), item 735
3. Andrew, B. E., *J. Anal. At. Spectrom.*, 1988, **3**, 401—405

A number of explosions have been experienced when using sample solutions containing perchloric acid in atomic absorption spectrometers using acetylene—nitrous oxide flames. Further information is being sought from other AAS users [1]. A warning against using perchloric acid digests in AA instruments using such flames has also been given by an American source [2]. The role of perchlorate accumulation and the effects of instrumental and experimental variables upon such explosions has been studied and preventive measures proposed [3].
See ATOMIC ABSORPTION SPECTROSCOPY

Alcohols MRH Ethanol 6.27/21
1. Sweasey, D., *Lab. Practice*, 1968, **17**, 915
2. Moureu, H. *et al., Arch. Mal. Prof. Med.*, 1951,**12**, 157—159
3. Michael, A. T. *et al., Amer. Chem. J.*, 1900,**23**, 444
4. Bailar, 1973, Vol. 2, 1451

During digestion of a lipid extract (1 mg) with 72% acid (1.5 ml), a violent explosion occurred. This was attributed to residual traces of the extraction solvent (methanol—chloroform) having formed methyl perchlorate [1]. In the analytical determination of potassium as perchlorate, heating the solid containing traces of ethanol and perchloric acid caused a violent explosion [2]. Contact of drops of anhydrous perchloric acid and

ethanol caused immediate violent explosion [3]. Partial esterification of polyfunctional alcohols (ethylene glycol, glycerol, pentaerythritol) with the anhydrous acid gives extremely explosive liquids which may explode on pouring from one vessel to another [4].
See Glycols and their ethers, below
See Methanol, Triglycerides, below
See ALKYL PERCHLORATES

Aniline, Formaldehyde MRH Aniline 6.65/18
Aniline, 86, New York, Allied Chem. Corp., 1964
Aniline reacts with perchloric acid and then formaldehyde to give an explosively combustible condensed resin.

Antimony(III) compounds
Burton, H. *et al., Analyst*, 1955, **80**, 4
Treatment of tervalent compounds of antimony with perchloric acid can be very hazardous.
See Bismuth, below

Azo-pigment, Orthoperiodic acid
1. Anon., *ABCM Quart. Safety Summ.*, 1961, **32**, 125
2. Smith, G. F. *et al., Talanta*, 1960, **4**, 185

During the later stages of the wet oxidation of an azo-pigment with mixed perchloric and orthoperiodic acids, a violent reaction, accompanied by flashes of light, set in and terminated in an explosion [1]. The general method upon which this oxidation was based is described as hazard-free [2].

Bis(1,2-diaminopropane)-*cis*-dichlorochromium(III) perchlorate
See Bis(1,2-diaminopropane)-*cis*-dichlorochromium(III) perchlorate: Perchloric acid

Bis(2-hydroxyethyl) terephthalate, Ethanol, Ethylene glycol
491M, 1975, 303
When a solution of the ester in ethanol containing 5% of perchloric acid was evaporated to dryness, there was a violent explosion (probably owing to formation of ethyl perchlorate, perhaps with some ester perchlorate or ethylene glycol perchlorate also being formed). A similar mixture containing ethylene glycol flashed brightly after refluxing for 18 h.
See Alcohols, above; Glycols and their ethers, below

Bismuth
Nicholson, D. G. *et al., J. Amer. Chem. Soc.*, 1935, **57**, 817
Attempts to dissolve bismuth and its alloys in hot perchloric acid carry a very high risk of explosion. At 110°C a dark brown coating is formed, and if left in contact with the acid (hot or cold), explosion occurs sooner or later. The same is true of antimony and its tervalent compounds.

Calcium compounds
Akerman, L. A. et al., *Combustion, Explos., & Shockwaves,* 1987, **23**, 178

Calcium chloride and oxide catalyse the second, violent, stage of ammonium perchlorate decomposition and increase the shock sensitivity of mixtures with sugar.

Carbon MRH 6.19/17

1. Mellor, 1941, Vol. 2, 380
2. Pascal, 1960, Vol. 16, 300—301

Contact of a drop of the anhydrous acid with wood charcoal causes a very violent explosion [1], and carbon black also reacts violently [2].

See Graphitic carbon, Nitric acid, below

Cellulose and derivatives MRH Cellulose 5.81/33

1. Schumacher, 1960, 187, 195
2. Harris, E. M., *Chem. Eng.*, 1949, **56**, 116
3. Sutcliffe, *J. Textile Ind.*, 1950, **41**, 196T

Contact of the hot concentrated acid or the cold anhydrous acid with cellulose (as paper, wood fibre or sawdust, etc.) is very dangerous and may cause a violent explosion. Many fires have been caused by long-term contact of diluted acid with wood (especially in fume cupboards) with subsequent evaporation and ignition [1,2]. Contact of cellulose acetate with 1200 l of uncooled anhydrous acid in acetic anhydride led to a particularly disastrous explosion [1], and interaction of benzyl cellulose with boiling 72% acid was also explosive [3]. Perchlorate esters of cellulose may have been involved in all these incidents.

See Hydrofluoric acid, Structural materials, below

Charcoal, Chromium trioxide

Randall, W. R., private comm., 1977

A wet-ashing technique used for dissolution of graphite in perchloric acid involved boiling a mixture of 70% perchloric acid and 1% of chromium trioxide as an aqueous solution. This method was later applied to 6—14 mesh charcoal, and after boiling for 30 min the reaction rate increased (foaming) and accelerated to explosion. The charcoal contained traces of extractable tar.

Clay

Atkinson, G. F., *Chem. Eng. News*, 1987, **65**(39), 2

Digestion of clay samples with perchloric acid led to 3 explosions, each of which destroyed a ceramic hotplate used as heat source. There seems a good case for using metal hotplates for reactions involving risk of explosion.

See Hydrogen peroxide: Acetic acid, Jute

Combustible materials

Elliot, M. A. *et al., Rept. Invest. No. 4169*, Washington, US Bur. Mines, 1948

Tests of sensitivity to initiation by heat, impact, shock or ignition sources were made on mixtures of a variety of absorbent materials containing a stoicheiometric amount of 40—70% perchloric acid. Wood meal with 70% acid ignited at 155°C and a mixture of coal and 60% acid which did not ignite below 200°C ignited at 90°C when metallic iron was added. Many of the mixtures were more sensitive and dangerous than common explosives.

Copper dichromium tetraoxide

Solymosi, F. *et al., Proc. 14th Combust. Symp.*, 1309—1316, 1973

The mixed oxide (copper chromite) was the most effective of several catalysts for the vapour-phase decomposition of perchloric acid, decomposition occurring above 120°C.

Dehydrating agents

1. Mellor, 1941, Vol. 2, 373, 380; 1956, Vol. 2, Suppl. 2.1, 598, 603
2. Kuney, J. H., *Chem. Eng. News*, 1947, **25**, 1659
3. Burton, H. *et al., Analyst*, 1955, **80**, 4
4. Schumacher, 1960, 71, 187, 193
5. Wirth, C. M. P., *Lab. Practice*, 1966, **15**, 675
6. Plesch, P.H. *et al., Chem. & Ind.*, 1971, 1043
7. Musso, H. *et al., Angew. Chem.*, 1970, **82**, 46

Although commercial 70—72% perchloric acid (approximating to the dihydrate) itself is stable, incapable of detonation (except by a booster charge) and readily stored, it may be fairly readily dehydrated to the anhydrous acid by contact with drying agents. This is not safe when stored at ambient temperature, since it slowly decomposes, even in the dark, with accumulation of chlorine dioxide in the solution, which darkens and finally explodes after some 30 days [1,2,5]. The 72% acid (or perchlorate salts) may be converted to the anhydrous acid by heating with sulfuric acid, phosphorus pentoxide or phosphoric acid, or by distillation under reduced pressure [1,4,5]. In contact with cold acetic anhydride, mixtures of the anhydrous acid with excess anhydride and acetic acid are formed, which are particularly dangerous, being sensitive to mechanical shock, heating, or the introduction of organic contaminants [2,3,4]. A solution of the monohydrated acid in chloroform exploded in contact with phosphorus pentoxide [1]. A safer method of preparing anhydrous solutions of perchloric acid in dichloromethane, which largely avoids the risk of explosion, has been described [6]. Further precautions are detailed in an account of an explosion during a similar preparation [7]. Solutions of anhydrous acid of less than 5% concentration in acetic acid or anhydride are relatively stable.

Deoxyribonucleic acid

Cochrane, A. R. G. *et al., School Sci. Rev.*, 1977, **58**, 706—708

Hazards of using perchloric acid to hydrolyse DNA are stressed. Perchloric acid can cause ignition of any organic material, even a considerable time after contact. Other acids to effect hydrolysis are suggested.

1,3-Di[bis(cyclopentadienyl)iron]-2-propene-1-one

See 1,3-Di[bis(cyclopentadienyl)iron]-2-propene-1-one: Perchloric acid

Dichloromethane, Dimethyl sulfoxide MRH Dimethyl sulfoxide 6.19/23

Anon., *Univ. Safety Assoc. Safety News*, 1978, (9), 10

When a syringe used for DMSO and rinsed with dichloromethane was being filled with perchloric acid, a violent explosion resulted.

See Sulfoxides, below

Diethyl ether MRH 6.61/18

Michael, A. T. *et al., Amer. Chem. J.*, 1900, **23**, 444

The explosions sometimes observed on contact of the anhydrous acid with ether are probably owing to formation of ethyl perchlorate by scission of the ether, (or possibly to formation of diethyloxonium perchlorate).

Dimethyl ether

See Acetonitrile, above

Dioxane, Nitric acid

MCA Guide, 1972, 312—313

Boron trifluoride in aqueous dioxane was being evaporated with nitric acid treatment (3 portions) for analysis. Final addition of perchloric acid with continued heating led to an explosion while unattended. Ring scission of dioxane to diethylene glycol and formation of diethylene glycol nitrate and/or perchlorate may have been involved.

See Nitric acid, Organic matter, below

Ethylbenzene, Thallium triacetate

Uemura, S. *et al., Bull. Chem. Soc., Japan.*, 1971, **44**, 2571

Application of a published method of thallation to ethylbenzene caused a violent explosion. A reaction mixture of thallium triacetate, acetic acid, perchloric acid and ethylbenzene was stirred at 65°C for 5 h, then filtered from thallous salts. Vacuum evaporation of the filtrate at 60°C gave a pasty residue which exploded. This preparation of ethylphenylthallic acetate perchlorate monohydrate had been done twice previously and uneventfully, as had been analogous preparations involving thallation of benzene, toluene, three isomeric xylenes and anisole in a total of 150 runs, where excessive evaporation had been avoided.

Faecal material, Nitric acid

Anon., *Univ. Safety Assoc. Safety News*, 1979, (12), 24

In the determination of metal ions in animal faeces, digestion with 12% perchloric and 56% nitric acids was in progress when an explosion occurred. This was attributed to one of the samples going to dryness on a sand tray heater.

See Nitric acid, Organic matter, below

Fluorine

Rohrbock, G. H. *et al., J. Amer. Chem. Soc.*, 1947, **69**, 677—678

Contact of fluorine and 72% acid at ambient temperature produces a high yield of the explosive gas, fluorine perchlorate.

Fume cupboards

1. Furr, A. K. (Ed.), *Handbook of Laboratory Safety*. 3rd Edn., 207, CRC Press, Boca Raton (Florida), 1990.
2. Bader, M. *et al., Appl. Occup. Environ. Hyg.*, 1999, **14**(6), 369
3. Kelly, R. J., *Chem. Health Saf.*, 2000, **7**(3), 5

Fume cupboards or their vent lines which have frequently been used with perchloric acid have often spontaneously deflagrated or exploded because of spillage or absorbed vapour [1]. Procedures for dismantling such systems have been developed [2,3].

See Hydrofluoric acid, Structural materials, below;
Cellulose and derivatives, above

Glycerol, Lead oxide

MCA Case History No. 799

During maintenance work on casings of fans used to extract perchloric acid fumes, seven violent explosions occurred when flanges sealed with lead oxide—glycerol cement were disturbed. The explosions, attributed to formation of explosive compounds by interaction of the cement with perchloric acid, may have involved perchlorate esters and/or lead salts. Use of an alternative inorganic silicate—hexafluorosilicate cement is recommended.

Glycols and their ethers MRH Ethylene glycol 5.69/30

1. Schumacher, 1960, 195, 214
2. Comas, S. M. *et al., Metallography*, 1974, **7**, 45—47

Glycols and their ethers undergo violent decomposition in contact with ~70% perchloric acid. This seems likely to involve formation of the glycol perchlorate esters (after scission of ethers) which are explosive, those of ethylene glycol and 3-chloro-1,2-propanediol being more powerful than glyceryl nitrate, and the former so sensitive that it explodes on addition of water [1]. Investigation of the hazards associated with use of 2-butoxyethanol for alloy electropolishing showed that mixtures with 50—95% of acid at 20°C, or 40—90% at 75°C, were explosive and initiable by sparks. Sparking caused mixtures with 40—50% of acid to become explosive, but 30% solutions appeared safe under static conditions of temperature and concentration.

See Alcohols, above

Graphitic carbon, Nitric acid

Buzzelli, G. *et al., Talanta*, 1977, **24**, 383—385

Dissolution procedures are described for gram samples of graphite or pyrolytic carbon, milligram samples of irradiated fuel particles, and for more readily oxidised forms of carbon, such as charcoal. The first two methods involve heating the samples with mixtures of 70% perchloric and 90% nitric acids (10:1), and must only be used for graphite or pyrolytic carbon. Other forms of carbon must not be oxidised in this way (to avoid explosions), but by a preliminary treatment with nitric acid alone and in portions.

See Carbon, above

Hydrofluoric acid, Structural materials

1. Anon., *Sichere Chemiearb.*, 1983, **35**, 85—86
2. Anon., *Sichere Chemiearb.*, 1984, **36**, 59

A violent explosion in a fume hood, in which inorganic siliceous materials had been digested with perchloric and hydrofluoric acids on a hotplate-heated sandbath during several years, originated from the tiled working surface. This consisted of ceramic tiles set in acid-proof organic resin-bond cement with mineral filler and supported on a 4 cm chipboard base. It appeared that prolonged use of the acids had led to development of hair cracks in the tiled surface, slow penetration of the acids into the underlying chipboard base and progressive formation of cellulose

perchlorate and other perchlorate esters from the resin binder beneath the tiled surface. The explosion was probably initiated by impact or friction, perhaps from moving the hotplate on the tiled surface. The significance of such factors in preventing such accidents is discussed [1]. A new piece of equipment should prevent the occurrence of such accidents caused by long-term use of perchloric acid. This is designed to accomodate 8 separate digestion vessels (PTFE for up to 250°C, other material in development for higher temperatures) heated in an aluminium block. Each vessel is connected by a PTFE line into a gas manifold which leads to an alkali-containing absorption vessel to completely neutralise the gases or vapours evolved during acid digestion [2].
See Cellulose and derivatives, above

Hydrogen

1. Dietz, W., *Angew. Chem.*, 1939, **52**, 616
2. Schumacher, 1960, 189

Occasional explosions experienced during use of hot perchloric acid to dissolve steel samples for analysis [1] were attributed to formation of hydrogen—perchloric acid vapour mixtures and their ignition by steel particles at temperatures as low as 215°C [2].

Hydrogen halides
See Fluoronium perchlorate
See also Chloronium perchlorate

Iodides
Michael, A. T. *et al., Amer. Chem. J.*, 1900, **23**, 444
The anhydrous acid ignites in contact with sodium iodide or hydriodic acid.

Iron(II) sulfate
Tod, H., private comm., 1968
During preparation of iron(II) perchlorate, a mixture of iron sulfate and perchloric acid was being strongly heated when a most violent explosion occurred. Heating should be gentle to avoid initiating this redox system.
See other REDOX REACTIONS

Ketones MRH Acetone 6.48/21
Schumacher, 1960, 195
Ketones may undergo violent decomposition in contact with 70% acid.

Methanol, Triglycerides

1. Mavrikos, P. J. *et al., J. Amer. Oil Chem. Soc.*, 1973, **50**(5), 174
2. Wharton, H. W., *J. Amer. Oil Chem. Soc.*, 1974, **51**(2), 35—36

Attention is drawn to the hazards involved in the use of perchloric acid in a published method [1] for transesterification of triglycerides with methanol. Alternative acid catalysts and safety precautions are suggested [2].

2-Methylpropene, Metal oxides
Lesnikovich, L. I. *et al., Chem. Abs.*, 1975, **83**, 149760; 1976, 85, 7929

Mixtures of the alkene and perchloric acid vapour (5:1 molar) in nitrogen ignite spontaneously at 250°C. Some metal oxides of low specific surface reduced the ignition temperature below 178°C.

Nitric acid, Organic matter

1. Anon., *Ind. Eng. Chem. (News Ed.)*, 1937, **15**, 214
2. Lambie, D. A., *Chem. & Ind.*, 1962, 1421
3. Mercer, E. R., private comm., 1967
4. Muse. L. A., *Chem. Eng. News*, 1973, **51**(6), 29—30
5. Cooke, G. W., private comm., 1967
6. Kuney, J. H., *Chem. Eng. News*, 1947, **25**, 1659
7. Balks, R. *et al., Chem. Abs.*, 1939, **33**, 2438.9
8. Rooney, R. C., *Analyst*, 1975, **100**, 471—475
9. Martinie, G. D. *et al., Anal. Chem.*, 1976, **48**, 70—74
10. *MCA Case History No. 2145*
11. Anon., *Univ. Safety Assoc. Safety News*, 1978, (9), 7
12. Satzger, R. D. *et al., J. Assoc. Off. Anal. Chem.*, 1983, **66**, 985—988
13. Frank, A., *Chem. Abs.*, 1983, **99**, 197442
14. Anon., *Lab. Accid Higher Educ.*, Item 15, HSE, Barking, 1987

The mixed acids have been used to digest organic materials prior to analysis, but several explosions have been reported, including those with vegetable oil [1], milk [2], and calcium oxalate precipitates from plants [3]. To avoid trace metal contamination by homogenising rat carcases in a blender, the whole carcases were dissolved in nitric acid. After separation of fat and addition of perchloric acid (125 ml), evaporation to near-dryness caused a violent explosion [4]. Finely ground plant material in contact with perchloric/nitric acid mixture on a heated sand bath became hot before all the plant material was saturated with acid and it exploded. Subsequent digests left overnight in contact with cold acids proceeded smoothly [5]. Cellulose nitrate and/or perchlorate may have been involved. Treatment with nitric acid before adding perchloric acid was a previously used and well-tried safe procedure [6]. Application to animal tissues of a method previously found satisfactory for plant material caused a violent explosion [7].

A method which involves gradually increasing the liquid temperature by controlled distillation during the digestion of organic matter with the hot mixed acids had been described as safe provided that strict control of the distillation process were observed [4]. During oxidation of large, high-fat samples of animal matter by the the usual technique, the existence of a layer of separated fat on the perchloric acid mixture created a highly hazardous situation. A modified procedure is free of explosion risk [8]. The effectiveness of mixed perchloric and nitric acids in wet oxidation of a wide range of organic materials has been studied. Violent oxidation occasionally occurred, but addition of sulfuric acid prevented any explosions or ignition during digestions [9]. The case history describes an explosion during wet-ashing of a phosphorus-containing polymer. One of the flasks may not have been topped up (i.e. diluted) with nitric acid during the digestion phase [10]. Digestion of vegetable matter with a 4:1 mixture of nitric/perchloric acids led to an explosion [11]. A safer alternative to the use of mixed acids for digestion of bone-meal for lead determination is pressurised dissolution in hydrochloric acid, then stripping voltammetry [12]. Equipment and procedures to minimise the risk of explosion during wet digestion of fat-containing materials are detailed [13]. An untried procedure to digest fresh cows milk with the mixed acids at 180°C led to a violent explosion [14].

Nitric acid, Pyridine, Sulfuric acid

Randall, W. L., *Safety in Handling Hazardous Chemicals*, 8—10, UCID-16610, Lawrence Livermore Lab., Univ. Calif., 1974

Some rare-earth fluoride samples had been wet-ashed incompletely with the three mixed acids and some gave low results. These samples, now containing pyridine, were reprocessed by addition of more acids and slow evaporation on a hot-plate. One of the samples frothed up and then exploded violently. Pyridinium perchlorate seems likely to have been involved.

Nitrogenous epoxides

Harrison, G. E., private comm., 1966

Traces of perchloric acid used as hydration catalyst for ring opening of nitrogenous epoxides caused precipitation of an organic perchlorate salt which was highly explosive. The concentration of acid was less than 1% by vol.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

Oleic acid

1. Swern, D. *et al.*, US Pat. 3 054 804; *Chem. Eng. News*, 1963, **41**(12), 39
2. Anon., *Chem. Eng. News*, 1963, **41**(27), 47

The improved preparation of 1,4-octadecanolactone [1] involves heating oleic acid (or other C_{18} acids) with 70% perchloric acid to 115°C. This is considered to be a potentially dangerous method [2].

Organic materials, Sodium hydrogen carbonate

1. Zderic, J. A. *et al., J. Amer. Chem. Soc.*, 1960,**82**, 446
2. Anon., *Univ. Safety Assoc. Safety News*, 1978, (9), 8—9

Following a published procedure [1], perchloric acid was used as catalyst in preparing a diol ketal, and was neutralised with sodium hydrogencarbonate before workup. Some sodium perchlorate remained dissolved after filtering the reaction mixture, and during subsequent vacuum distillation (with the bath temperature increasing to 200°C) an explosion occurred.

Organophosphorus compounds

Anderson, R. L. *et al., Clin. Chim. Acta*, 1982, **121**, 111—116

The standard method for assaying organophosphorus compounds can be modified to use sulfuric acid to digest the samples and hydrogen peroxide as oxidant in place of perchloric acid.

Other reactants

Yoshida, 1980, 78

MRH values calculated for 19 combinations with oxidisable materials are given.

Paper, Silver compounds

Demer, F. R., *University of Arizona Lab. Safety Notes*, 1994, spring

Perchloric acid and paper towels were used to clean up a silver nitrate stain. After placing in a waste bin, the towels ignited.

Phenylacetylene

1. Martheard, J.-P. *et al., Tetrahedron Lett.*, 1982,**23**, 3484
2. Martheard, J.-P. *et al., J. Chem. Res., Synop.*, 1983, 224—225

A mixture of phenylacetylene and the pure (?anhydrous) acid prepared at —180°C exploded when allowed to warm to —78°C, possibly owing to formation of unstable 1-phenylethenyl perchlorate [1]. Reaction of various phenylacetylenes in acetic acid at 40°C is controllable [2].

Phosphine

See Phosphonium perchlorate

Pyridine

See Pyridinium perchlorate

Sodium phosphinate MRH 3.68/63

Smith, G. F., *Analyst*, 1955, **80**, 16

Although no interaction occurs in the cold, these powerful oxidising and reducing agents violently explode on heating.

See other REDOX REACTIONS

Sulfinyl chloride

Bailar, 1973, Vol. 2, 1442

The anhydrous acid ignites the chloride.

Sulfoxides MRH Dimethyl sulfoxide 6.19/23

1. Therésa, J. de B., *Anales Soc. Espan. Fis. y Quim.*, 1949, **45B**, 235
2. Graf, F. A., *Chem. Eng. Progr.*, 1966, **62**(10), 109
3. Uemura, S. *et al., Bull. Chem. Soc. Japan*, 1971, **44**, 2571
4. *471M*, 1975, 302
5. Anon., *Jahresber.*, 1990, 64
6. Eigenmann, K. *et al., Angew. Chem. (Intern. Ed.)*, 1975, **14**, 647—648

Lower members of the series of salts formed between organic sulfoxides and perchloric acid are unstable and explosive when dry. That from dibenzyl sulfoxide explodes at 125°C [1]. Dimethyl sulfoxide explodes on contact with 70% perchloric acid solution [2]; one drop of acid added to 10 ml of sulfoxide at 20°C caused a violent explosion [3], and dibutyl sulfoxide behaves similarly [4]. A fatal explosion resulted from mistakenly connecting a DMSO reservoir to an autopipette previously used with perchloric acid [5]. (The editor has met a procedure for methylthiolation of aromatics where DMSO was added to excess 70% perchloric acid; he did not feel justified in trying to scale it up.) Explosions reported seem usually to result from addition to excess sulfoxide. Aryl sulfoxides condense uneventfully with phenols in 70% perchloric acid, but application of these conditions to the alkyl sulfoxide (without addition of the essential phosphoryl chloride) led to a violent explosion [4]. Subsequent investigation showed that mixtures of phenol and perchloric acid are thermally unstable (ester formation?) and may decompose violently, the temperature range depending on composition. DSC measurements showed that sulfoxides alone

may decompose violently at elevated temperatures; e.g. dimethyl sulfoxide, 270—355, cyclohexyl methyl sulfoxide, 181—255, or methyl phenyl sulfoxide, 233—286°C, respectively [6].
See Dimethyl sulfoxide: Metal oxosalts

Sulfur trioxide
Pascal, 1960, Vol. 16, 301
Interaction of the anhydrous acid and sulfur trioxide is violent and highly exothermic, even in presence of chloroform as diluent, and explosions are frequent.
See Dehydrating agents, above

Sulfuric acid, Organic materials
Young, E. G. *et al., Science* (New York), 1946, **104**, 353
Precautions are necessary to prevent explosions when using the mixed acids to oxidise organic materials for subsequent analysis. The sulfuric acid probably tends to dehydrate the 70% perchloric acid to produce the hazardous anhydrous acid.
See Nitric acid, etc., above

Trichloroethylene
Prieto, M. A. *et al., Research on the Stabilisation and Characterisation of Highly Concentrated Perchloric Acid*, 36, Whittier, Calif., American Potash and Chem. Corp., 1962
The solvent reacts violently with the anhydrous acid.

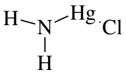
Trimethylplatinum hydroxide
See Dodecamethyltetraplatinum(IV) perchlorate

Vegetable matter
Tabatabai, M. A. *et al., Agron. J.*, 1982, **74**, 404—406
As a safer alternative to digestion of vegetable matter with perchloric acid, alkaline oxidation of sulfur compounds to sulfate by sodium hypobromite, and reduction of sulfate to hydrogen sulfide by hydriodic acid/formaldehyde/phosphinic acid is recommended.
See Sulfuric acid, Organic materials, above

Zinc phosphide
Muir, G. D., private comm., 1968
Use of perchloric acid to assist solution of a sample for analysis caused a violent reaction.
See other INORGANIC ACIDS, OXIDANTS, OXOHALOGEN ACIDS, REDOX REACTIONS

3993. Mercury(II) amide chloride

[10124-48-8] **ClH_2HgN**



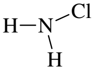
Halogens
Schwarzenbach, V., *Ber.*, 1875, **8**, 1231—1234

Several min after addition of ethanol to a mixture of the amide chloride ('fusible white precipitate') and iodine, an explosion occurs. Addition of the compound to chlorine gas or bromine vapour leads to a delayed violent or explosive reaction. Amminemetal salts behave similarly, and formation of *N*-halogen compounds is involved in all cases.

See other MERCURY COMPOUNDS, N-METAL DERIVATIVES

3994. Chloramine (Chloramide)

[10599-90-3] **ClH_2N**



1. Marckwald, W. *et al., Ber.*, 1923, **56**, 1323
2. Coleman, G. H. *et al., Inorg. Synth.*, 1939, **1**, 59
3. Walek, W. *et al., Tetrahedron*, 1976, **32**, 627

The solvent-free material, isolated at —70°C, disproportionates violently (sometimes explosively) at —50°C to ammonium chloride and nitrogen trichloride [1]. Ethereal solutions of chloramine are readily handled [2]. In the preparation of chloramine by reaction of sodium hypochlorite with ammonia, care is necessary to avoid excess chlorine in the preparation of the hypochlorite from sodium hydroxide, because nitrogen trichloride may be formed in the subsequent reaction with ammonia [3].

See other N-HALOGEN COMPOUNDS

3995. Ammonium chloride

[12125-02-9] **ClH_4N**

HCS 1980, 142

1. Alfenaar, M. *et al.*, Neth. Appl. 73 07 035, 1974
2. Knothe, M., *Schriftenr. GDMB*, 1998, (82), 101

Ammonium chloride is generally inoffensive. However, subjected to oxidation, especially electrochemically, it has the potential to form nitrogen trichloride. Cyanogen halides may be prepared by electrolysis of hydrogen cyanide or its salts mixed with halide salts. If ammonium chloride is used as the halide salt, precautions to prevent formation of explosive nitrogen trichloride are necessary [1]. Nitrogen trichloride is an under-recognised hazard of electrolytic operations in hydrometallurgy, where it may appear at pH < 9 from electrolysis of ammonium or amine salts in chloride electrolytes [2].

See ELECTROLYSIS

Interhalogens

See Bromine trifluoride: Ammonium halides

Bromine pentafluoride: Acids, etc.

Other reactants

Yoshida, 1980, 53

MRH values calculated for 10 combinations with various reagents are given.

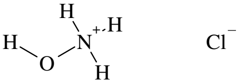
Potassium chlorate MRH MRH 1.46/60

See Potassium chlorate: Ammonium chloride

See related METAL HALIDES

3996. Hydroxylaminium chloride

[5470-11-1] **ClH_4NO**



FPA H66, 1978

Manganese dioxide

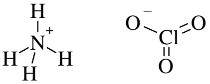
Chaterjee, B. P. *et al., Talanta*, 1977, **24**, 180—181

In a method for titrimetric determination of manganese in pyrolusite ore, addition of the powdered ore to a cold 20% solution of the salt causes vigorous decomposition to occur.

See entry HYDROXYLAMINIUM SALTS

3997. Ammonium chlorate

[10192-29-7] **ClH_4NO_3**



1. Brauer, 1963, Vol. 1, 314
2. Urbanski, 1965, Vol. 2, 476

It occasionally explodes spontaneously, and invariably above 100°C [1]. It will explode after 11 h at 40°C, and after 45 min at 70°C. Ammonium and chlorate salts should not be mixed together [2].

Water

Mellor, 1941, Vol. 2, 339; 1956, Vol. 2, Suppl. 1, 591

A cold saturated solution may decompose explosively after a few days if much excess solid is present. Hot aqueous solutions have exploded during evaporation in steam heated vessels.

See other OXOSALTS OF NITROGENOUS BASES

3998. Ammonium perchlorate
[7790-98-9] **ClH_4NO_4**

1. *MCA Case History No. 1002*
2. Barret, P., *Cah. Therm.*, 1974, **4**, 13—22
3. Seltzer R. J., *Chem. Eng. News*, 1988, **66**(32), 7
4. Olson, D. B. *et al., Chem. Abs.*, 1999, **130**, 211435m
5. Langerman, N., Private communication, 2001

Materials for a batch of ammonium perchlorate castable propellant were charged into a mechanical mixer. A metal spatula was left in accidentally, and the contents ignited when the mixer was started, owing to local friction caused by the spatula. A tool-listing safety procedure was instituted [1]. The literature on the kinetics of thermal decomposition has been reviewed critically [2]. More refined thermal stability studies show some large differences from earlier ones [4].

For an account of the destruction of a plant producing ammonium perchlorate, which was not generally considered to be explosive, see [3]. Below 400°C it behaves as an oxidising agent but decomposition is not violent. The event suggests that tonnage quantities can detonate in some circumstances. The fire was started in spilt waste by sparks from welding and spread to storage areas on asphalt (fuel!); two aluminium bins, each containing five tonnes of perchlorate then detonated [3]. Further investigation suggested that initiation was actually from deflagration of ammonium perchlorate dust contaminating the insulation of a drying oven, which had happened previously. Incubation at 150°C for 100 hours will cause a runaway[5].

Aluminium MRH 9.99/27

Loftus, H. J. *et al., Rept. AD-769283/3GA*, 1—98, Springfield (Va.), USNTIS, 1973

The powdered solid materials have been evaluated as a practical propellant pair.

Carbon MRH 4.52/9

Galwey, A. K. *et al., Trans. Faraday Soc.*, 1960, **56**, 581

Below 240°C intimate mixtures with sugar charcoal undergo exothermic decomposition, while mild explosions occur above 240°C.

Catalysts

1. Solymosi, F., *Acta Phys. Chem.*, 1974, **20**, 83—103
2. Shadman-Yazdi, F., *Proc. 1973 Iran. Congr. Chem. Eng.*, 1974, **1**, 353—356
3. Glazkova, A. P., *Chem. Abs.*, 1976, **85**, 162846
4. Rastogi, R. P. *et al., J. Appl. Chem. Biotechnol.*, 1978, **28**, 889—894

In a review of the course and mechanism of the catalytic decomposition of ammonium perchlorate, the considerable effects of metal oxides in reducing the explosion temperature of the salt are described [1]. Solymosi's previous work had shown reductions from 440° to about 270° by dichromium trioxide, to 260° by 10 mol% of cadmium oxide and to 200°C by 0.2% of zinc oxide. The effect of various concentrations of 'copper chromite', copper oxide, iron oxide and potassium permanganate on the catalysed combustion of the propellant salt was studied [2]. Similar studies on the effects of compounds of 11 metals and potassium dichromate in particular, have been reported [3]. Presence of calcium carbonate or calcium oxide has a stabilising effect on the salt, either alone or in admixture with polystyrene [4].

Copper MRH 2.17/57

Anon., *Chem. Engrg.*, 1955, **62**(12), 335

Crystalline ammonium perchlorate ignited in contact with hot copper pipes.

Ethylene dinitrate

MCA Case History No. 1768

Samples of mixtures of ammonium perchlorate and the highly explosive liquid nitrate kept at 60°C ignited after 7 days. Many adverse criticisms of the general planning and execution of the experiments were made.

Impurities

1. Jacobs, P. W. M. *et al., Chem. Rev.*, 1969, **69**, 590
2. Jain, S. R. *et al., Combust. Flame*, 1981, **40**, 113—120

The medium impact-sensitivity of this solid propellant component is greatly increased by co-crystallisation of certain impurities, notably nitryl perchlorate, potassium periodate and potassium permanganate [1]. The presence of certain minimum amounts of mono-, di, tri- or tetra-methylammonium perchlorates in the salt leads to a single step decomposition, at around 290°C for the mono-derivative [2].

See other CATALYTIC IMPURITY INCIDENTS

Metal perchlorates

1. Solymosi, F., *Combust. Flame*, 1966, **10**, 398—399
2. Solymosi, F., *Z. Phys. Chem.*, 1969, **67**, 76—85
3. Patel, K. C. *et al., Combust. Flame*, 1976, **27**, 295—298
4. Al Fakir, M. S., *Progr. Astronaut. Aeronaut.*, 1981, **76**, 5512—564

Admixture of lithium perchlorate [1] or zinc perchlorate [2] leads to decomposition with explosion at 290° or ignition at 240°C, respectively. The role of ammine derivatives of lithium and magnesium perchlorates in catalysing the thermal decomposition of ammonium perchlorate has been studied [3], and lithium perchlorate has a strong catalytic effect on the burning rate [4].

Metals, or Organic materials, or Sulfur MRH Magnesium 12.97/49/Sulfur 3.59/27

1. *Haz. Chem. Data*, 1975, 51
2. Klager, K. *et al., Chem. Abs.*, 1982, **97**, 94903

The powdered oxidant functions as an explosive when mixed with finely divided metals, organic materials or sulfur, which increase the shock-sensitivity up to that of picric acid [1]. The hazardous properties of such mixtures increase as the particle size of the oxidant salt decreases [2].

Nitrophenol—formaldehyde polymer

Girdhar, H. L. *et al., Indian J. Technol.*, 1981, **19**, 531—532

The combination (or one with potassium perchlorate) is an explosive propellant.

Other reactants

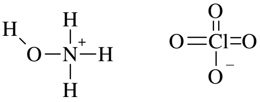
Yoshida, 1980, 79

MRH values calculated for 19 combinations with oxidisable materials are given.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

3999. Hydroxylaminium perchlorate

[15588-62-2] **ClH_4NO_5**



1. Rafeev, V. A. *et al., Chem. Abs.*, 1981, **95**, 83166
2. Bokii, V. A. *et al., Chem. Abs.*, 1981, **94**, 49734

The decomposition and combustion of the redox salt [1], and its mechanism [2] were studied.

1,3,5-Triaminotrinitrobenzene

Quong, R., *Chem. Abs.*, 1975, **82**, 113753

A saturated aqueous solution of the perchlorate, and the solid fuel, are individually non-explosive, but form a viable explosive composition on admixture.

See other PERCHLORATE SALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

4000. Phosphonium perchlorate

[101672-21-3] **ClH_4O_4P**

1. Fichter, F. *et al., Helv. Chim. Acta*, 1934, **17**, 222
2. Mellor, 1971, Vol. 8, Suppl. 3, 274

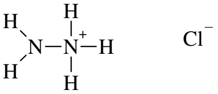
The crystalline salt obtained by action of phosphine on 68% perchloric acid at —20°C is dangerously explosive, sensitive to moist air, increase in temperature, or friction [1] and cannot be dried [2].

See other REDOX COMPOUNDS

See related PERCHLORATE SALTS OF NITROGENOUS BASES

4001. Hydrazinium chloride

[2644-70-4] **ClH_5N_2**

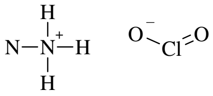


See entry THERMAL EXPLOSIONS

See other HIGH-NITROGEN COMPOUNDS

4002. Hydrazinium chlorite

[66326-45-2] **$ClH_5N_2O_4$**



Levi, G. R., *Gazz. Chim. Ital. [2]*, 1923, **53**, 105—108

It is spontaneously flammable when dry.

See other CHLORITE SALTS, REDOX COMPOUNDS

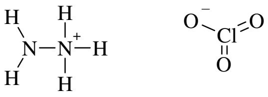
4003. Ammonium perchlorylamide

[20394-65-4] **$ClH_5N_2O_3$**

See entry PERCHLORYLAMIDE SALTS

4004. Hydrazinium chlorate

[66326-46-3] **$ClH_5N_2O_3$**



Salvadori, R., *Gazz. Chim. Ital. [2]*, 1907, **37**, 32—40

It explodes violently at its m.p., 80°C.

See other OXOSALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

4005. Hydrazinium perchlorate

[13762-80-6] **$ClH_5N_2O_4$**

1. Levy, J. B. *et al., ACS 54*, 1966, 55
2. Grelecki, C. J. *et al., ACS 54*, 1966, 73
3. Salvadori, R., *Gazz. Chim. Ital. [2]*, 1907, **37**, 32—40

The deflagration [1] and thermal decomposition [2] of the salt, a component of solid rocket propellants, have been studied. It also explodes on impact [3].

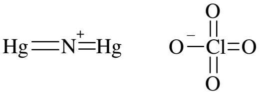
Metal salts, or Metal oxides

1. Shidlovskii, A. A. *et al., Zh. Priklad. Chim.*, 1962, **35**, 756
2. Probhakaran, C. *et al., Def. Sci. J.*, 1982, **31**, 285—291

Presence of 5% of copper(II) chloride caused explosion to occur at 170°C [1]. Of the series of additives copper chromite, copper chloride, nickel oxide, iron oxide, magnesium oxide, the earlier members have the greatest effect in increasing the sensitivity of the perchlorate to heat, impact and friction.
See other PERCHLORATE SALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

4006. Poly(dimercuryimmonium perchlorate)

[ ] **$(ClHg_2NO_4)_n$**



$$Hg{=}\overset{+}{N}{=}Hg \qquad \overset{-}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cl}}{=}O$$

Sorbe, 1968, 97
Highly explosive.
See other PERCHLORATE SALTS OF NITROGENOUS BASES, POLY(DIMERCURYIMMONIUM) COMPOUNDS

4007. Iodine chloride

[7790-99-0] **ClI**

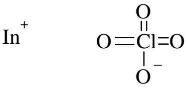
$I{-}Cl$

Metals
Mellor, 1940, Vol. 2, 119; 1956, Vol. 2, Suppl. 1, 452; 1963, Vol. 2, Suppl. 2.2, 1563
Mixtures containing sodium explode only on impact, while potassium explodes on contact with the chloride. Aluminium foil ignites after prolonged contact (probably after the surface layer of oxide has been dissolved).

Phosphorus trichloride
Mellor, 1956, Vol. 2, Suppl. 1, 502
Reaction is intensely exothermic.
See other INTERHALOGENS, IODINE COMPOUNDS

4008. Indium(I) perchlorate

[62763-56-8] **$ClInO_4$**



$$In^{+} \qquad O{=}\overset{\overset{O}{\|}}{\underset{\underset{O^{-}}{|}}{Cl}}{=}O$$

Ashraf, M. *et al., J. Chem. Soc., Dalton Trans.*, 1977, 1723
The solvent-free material detonated when crushed with a glass rod. The nitrate (also a redox compound) probably would behave similarly.
See other METAL PERCHLORATES, REDOX COMPOUNDS

4009. Potassium chloride

[7447-40-7] **ClK**

K^+ Cl^-

Nitrogenous compounds

Saraf, P. C., *Chem. Eng. World (India)*, 1998, **33**(11), 179

As with other chlorides electrolysis can give rise to nitrogen trichloride. The anticaking agents used on commercial potassium chloride may be nitrogenous. Purification methods for potassium hydroxide manufacture are discusssed.

See Nitrogen trichloride

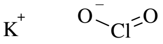
Potassium permanganate, Sulfuric acid

See Potassium permanganate: Potassium chloride, etc.

See other METAL HALIDES

4010. Potassium chlorite

[14314-27-3] **$ClKO_2$**



Other reactants

Yoshida, 1980, 3

MRH values calculated for 18 combinations with oxidisable materials are given.

Sulfur MRH 3.22/13

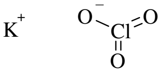
Leleu, *Cahiers*, 1974, (74), 137

Interaction is violent.

See other CHLORITE SALTS

4011. Potassium chlorate

[3811-04-9] **$ClKO_3$**



HCS 1980, 762

1. Rüst, 1948, 294
2. Biasutti, 1981, 151
3. Anon., *Fire Prevention*, 1986, (186), 48
4. Cardillo. P., *J. Loss Prev. Proc. Ind.*, 2000, **14**, 69
5. Baldwin, M. et al., *Chem. World*, 2004, **1**(11), 29

Although most explosive incidents have involved mixtures of the chlorate with combustible materials, the exothermic decomposition of the chlorate to chloride and oxygen can accelerate to explosion if a sufficient quantity and powerful enough heating are involved. A case history of a fire-heated explosion of a store of 80 t of chlorate is given. The more stable sodium chlorate will also explode under similar conditions [1]. The enthalpy of conversion of potassium chlorate to either chloride or perchlorate is slight, about ¼kJ/g, less than is the case for the sodium salt. During sieving of the dry chlorate in a store attached to a fuse igniter plant, a violent explosion of 75 kg of the salt occurred. It seems likely that some oxidisable material was involved in the incident, though the possibility of dropping a drum onto the concrete floor is noted as a potential cause of ignition [2]. An account of an explosion of 16 tonnes during a fire in a warehouse, demolishing 100 metres of the wall is given. The chlorate does not seem to have been isolated from other goods [3]. Although sulfur and charcoal were usually involved in the several fatal explosions attendant upon the late 18th century attempt to replace potassium nitrate by potassium chlorate in manufacture of black powder, in one instance chlorate alone seems to have exploded [4].

Various anecdotal accounts are given of incendiary mishaps consequent upon former use of chlorate throat lozenges [5].

Agricultural materials
See Sodium chlorate: Agricultural materials

Aluminium,
MRH 9.20/30

Ammonia, or Ammonium sulfate MRH Ammonia 4.23/21
Mellor, 1941, Vol. 2, 702; 1940, Vol. 8, 217
High concentrations of ammonia in air react so vigorously with potassium chlorate as to be dangerous. Mixtures with ammonium sulfate when heated decompose with incandescence.

Ammonium chloride
1. Potjewijd, T., *Pharm. Weekbl.*, 1935, **72**, 68—69
2. Ellern, 1968, 155

Addition of ammonium chloride to a drum of weed-killer was suspected as the cause of a violent explosion (involving formation of ammonium chlorate) [1]. Mixtures, used for smoke compositions, are hazardous [2].

Antimony trisulfide MRH 2.84/39
Crozier, T. H. *et al., 52nd Ann. Rept. HM Insp. Explos.*, London, Home Office, 1928
A pyrotechnic mixture containing the powdered ingredients was found dangerously sensitive to frictional initiation and highly explosive.
See Metal sulfides, below
See Metals, below

Aqua regia, Ruthenium
Sidgwick, 1950, 1459
Ruthenium is insoluble in aqua regia, but addition of potassium chlorate causes explosive oxidation.

Arsenic trisulfide
Ganguly, A., *J. Indian Acad. Forensic Sci.*, 1973, **12**, 29—30

Dry powdered mixtures containing over 30% oxidant exploded under a hammer-blow.
See Metal sulfides, below

Carbon MRH 4.52/13
Read, C. W. W., *School Sci. Rev.*, 1941, **22**(87), 341
Accidental substitution of powdered carbon for manganese dioxide in 'oxygen mixture' caused a violent explosion when the mixture was heated.

Cellulose
1. Watanabe, M. *et al., Chem. Abs.*, 1988, **108**, 207227
2. Ishida, H. *et al., Chem. Abs.*, 1988, **109**, 56797

Mixtures of stoichiometric proportions (zero oxygen balance) are a high deflagration hazard and show remarkable pressure increase effects on ignition [1], as well as lowest ignition temperatures by ARC [2].
See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 4)

Charcoal, Potassium nitrate, Sulfur
Biasutti, 1981, 4
A batch of black powder, modified by addition of potassium chlorate, was being mixed mechanically with added water. A friction-sensitive crust appears to have formed, leading to initiation of the explosion which followed.
See Non-metals, below

Charcoal, Sulfur
Biasutti, 1981, 15, 42, 46
A demonstration by Berthollet in 1788 of replacement of potassium nitrate in gunpowder by the chlorate led to a violent explosion during the crushing operation which caused two fatalities. Later incidents involving factories for chlorate-containing explosives led to widespread destruction.

Cyanides
See METAL CYANIDES (AND CYANO COMPLEXES) (reference 1)

Cyanoguanidine
See Cyanoguanidine: Oxidants

Dinickel trioxide
Mellor, 1942, Vol. 15, 395
Interaction at 300°C is violently exothermic, red heat being attained.

Fabric
Anon., *Accidents*, 1968, 24
Fabric gloves (wrongly used in place of impervious plastics gloves) became impregnated during handling operations and were subsequently ignited from cigarette ash.
See Cellulose, above

Fluorine
Pascal, 1960, Vol. 16, 316

Interaction at low pressure leads to formation of the explosive gas, fluorine perchlorate.
See Fluorine: Sodium bromate

Gallic acid, Gum tragacanth
Anon., *Lab. Accid. Higher Educ.*, item 7, Barking, HSE, 1987
A 'pyrotechnic device' was being prepared by loading 16 g of a mixture of 73% potassium chlorate, 24% gallic acid and 3% gum tragacanth into a 9 mm copper tube 280 mm long, when it exploded violently and caused shrapnel injuries. Such mixtures are very friction-sensitive.

Hydrocarbons MRH Hexane 4.77/10, Toluene 4.81/12
1. Bjorkman, P. O., *Chem. Abs.*, 1934, **28**, 6311a
2. von Feilitzen, G., *Chem. Abs.*, 1934, **28**, 6311b

Mixtures of powdered chlorate and hydrocarbons explode as violently as nitro compound explosives [1]. Porous masses of chlorate impregnated with hydrocarbons are friction-sensitive explosives [2].

Hydrogen iodide
Mellor, 1941, Vol. 2, 310
Molten potassium chlorate ignites hydrogen iodide gas.

Manganese dioxide
1. Mellor MIC, 1961, 333
2. Partington, 1967, 651
3. Renfrew, M. M., *J. Chem. Educ.*, 1983, **60**, A229

When oxygen is generated in the laboratory by heating potassium chlorate with manganese dioxide as decomposition catalyst, the latter must be free of organic matter or an explosion will occur [1]. The mixture (17% wt of manganese dioxide, 'oxygen mixture') must be cautiously heated at 250°C with a small flame to prevent the exothermic decomposition reaction becoming violent [2]. Mixing the components dry with a partially plastic-coated micro-spatula caused a fire [3].
See other CATALYTIC IMPURITY INCIDENTS

Manganese dioxide, Potassium hydroxide
Molinari, E. *et al., Inorg. Chem.*, 1964, **3**, 898
The oxidation of manganese dioxide to manganate by solid alkali—chlorate mixtures becomes explosive above 80—90°C at pressures above 19 kbar.

Metal phosphides
Mellor, 1940, Vol. 8, 839, 844
Tricopper diphosphide and trimercury tetraphosphide form impact-sensitive mixtures with potassium chlorate. By analogy, the phosphides of aluminium, magnesium, silver and zinc, etc., would be expected to form similar mixtures with metal halogenates.

Metal phosphinates ('hypophosphites')
Mellor, 1940, Vol. 8, 881, 883

Dry mixtures of barium phosphinate and potassium chlorate burn rapidly with a feeble report if unconfined, but even under the slight confinement of enclosing in paper, a sharp explosion occurs. The mixture is readily initiated by sparks, impact or friction. A mixture of calcium phosphinate, potassium chlorate and quartz exploded during mixing. Mixtures of various phosphinates and chlorates have been proposed as explosives, but they are very sensitive to initiation by sparks, friction or shock. Admixture of powdered magnesium causes a brilliant flash on initiating the mixture.
See Sodium phosphinate: Oxidants
See other FRICTIONAL INITIATION INCIDENTS, STATIC INITIATION INCIDENTS

Metal sulfides MRH Antimony trisulfide 2.34/39, silver sulfide 1.38/62

1. Mellor, 1941, Vol. 2, 310
2. Mellor, 1939, Vol. 9, 523
3. Mellor, 1941, Vol. 3, 447
4. Rüst, 1948, 335

Many metal sulfides when mixed intimately with metal halogenates form heat-, impact- or friction-sensitive explosive mixtures [1]. That with antimony trisulfide can be initiated by a spark [2] and with silver sulfide a violent reaction occurs on heating [3]. For the preparation of ‘oxygen mixture’, antimony trisulfide was used in error instead of manganese dioxide, and during grinding, the mixture of sulfide and chlorate exploded very violently [4].
See also METAL HALOGENATES

Metal thiocyanates

1. von Schwartz, 1918, 299—300
2. Anon., *Chem. Age.*, 1936, **35**, 42

Mixtures of thiocyanates with chlorates (or nitrates) are friction- and heat-sensitive, and explode on rubbing, heating to 400°C, or initiation by spark or flame [1]. A violent explosion occurred when a little chlorate was ground in a mortar contaminated with ammonium thiocyanate. A similar larger-scale explosion involving traces of barium thiocyanate is also described [2].

Metal, Wood

Davis, G. C., *J. Ind. Eng. Chem.*, 1909, **1**, 118
Explosions were caused by transportation of metal castings in wooden kegs previously used to store potassium chlorate, impact or friction of the metal causing initiation of the chlorate-impregnated wood.

Metals MRH Aluminium 9.20/30, magnesium 9.50/37, iron 3.64/47

1. Mellor, 1941, Vol. 2, 310
2. Anon., *Chem. Eng. News*, 1936, **14**, 451
3. Mellor, 1940, Vol. 4, 480
4. Mellor, 1943, Vol. 11, 163
5. Mellor, 1941, Vol. 7, 20, 116, 260
6. Jackson, H., *Spectrum*, 1969, **7**, 82
7. Ganguly, A., *J. Indian Acad. Forensic Sci.*, 1973, **12**, 29—30

Mixtures of finely divided aluminium, copper, magnesium [1,2] and zinc [3] with potassium chlorate (or other metal halogenates) are explosives and may be initiated by heat, impact or light friction. Chromium incandesces in the molten salt [4] and germanium explodes on heating with potassium chlorate. Titanium explodes on heating, while zirconium gives mild explosions on heating, and ignites when the mixture is impacted [5]. Contact of molten chlorate with steel wool causes violent combustion of the latter [6]. Qualitative experiments showed that hammer impact would explode mixtures with aluminium powder containing over 10% of chlorate [7].

See also FLASH POWDER

See other METAL CHLORATES, METAL OXOHALOGENATES

Nitric acid, Organic materials

Asthana, S. S. *et al., Chem. & Ind.*, 1976, 953—954

In a new method of degrading organic matter prior to analysis, small portions (0.3 g only) of chlorate are added to a hot suspension of the organic matter in conc. nitric acid. Use of larger portions of chlorate may lead to explosive oxidation of the organic matter.

Non-metals MRH Carbon 4.52/13, phosphorus 5.98/23, sulfur 3.18/18

1. Mellor, 1941, Vol. 2, 310
2. Mellor, 1940, Vol. 8, 785—786
3. Mellor, 1946, Vol. 5, 15
4. Ganguly, A., *J. Indian Acad. Forensic Sci.*, 1973, **12**, 29—30

Potassium chlorate (or other metal halogenate) intimately mixed with arsenic, carbon, phosphorus, sulfur or other readily oxidised materials gives friction-, impact- and heat-sensitive mixtures which may explode violently [1]. When potassium chlorate is moistened with a solution of phosphorus in carbon disulfide, it eventually explodes as the solvent evaporates and oxidation proceeds [2]. Boron burns in molten chlorate with dazzling brilliance [3]. Mixtures of the chlorate and finely powdered sulfur containing over 20% of the latter will explode under a hammer-blow [4].

See Sulfur, below

See also METAL HALOGENATES

See other METAL CHLORATES

Other reactants

Yoshida, 1980, 65—66

MRH values calculated for 24 combinations with oxidisable materials are given.

Phosphorus (red)

1. Haarmann, D. J., *American Fireworks News*, 1985, #51; *ibid.*, 1986, #54,
2. *Explosives and Their Power*, Berthelot, M., (translated and condensed from the French), London, 1892

This combination has, in the past, been the base of various impact sensitive pyrotechnics, described by Haarmann [1] and more recently on the Internet, including reference to a report [2] of a mere 60—70 kg, dispersed in children's toy caps, demolishing a building in an accidental explosion. Red phosphorus is a material of variable composition and reactivity, so unreliability is to be anticipated. There have been passivating components in most of these mixtures, it is suggested that the pure dry powders will often react on contact. For the more reactive white allotrope:

See Non-metals, above

Reducants

Mellor, 1941, Vol. 3, 651; 1940, Vol. 8, 881, 883

Mixtures with calcium hydride or strontium hydride may explode readily, and interaction of the molten chlorate is, of course, violent. A mixture of syrupy sodium phosphinate ('hypophosphite') and the powdered chlorate on heating eventually explodes as powerfully as glyceryl nitrate. Calcium phosphinate mixed with the chlorate and quartz detonates (the latter producing friction to initiate the mixture). Dried mixtures of barium phosphinate and the chlorate are very sensitive and highly explosive under the lightest confinement (screwed up in paper).

Sodium amide MRH 2.63/24

Mellor, 1940, Vol. 8, 258

A mixture explodes.

Sugar, Sulfuric acid

Hanson, R. M., *J. Chem. Educ.*, 1976, **53**, 578

Addition of a drop of sulfuric acid to a mound of the chlorate—sugar mixture leads to ignition.

Sugars

1. Zaehringer, A. J., *Rocketscience*, 1949, **3**, 64—68
2. Ganguly, A., *J. Indian Acad. Forensic Sci.*, 1973, **12**, 29—30
3. Scanes, F. S., *Combust. Flame*, 1974, **23**, 363—371

A stoicheiometric mixture with sucrose ignites at 159°C, and has been evaluated as a rocket propellant [1]. Dry powdered mixtures with glucose containing above 50% of chlorate explode under a hammer-blow [2]. Pyrotechnic mixtures with lactose begin to react exothermally at about 200°C, when the lactose melts, and carbon is formed. This is then oxidised by the chlorate at about 340°C. The mechanism was studied by DTA [3].

Sulfur MRH 3.18/18

1. Tanner, H. G., *J. Chem. Educ.*, 1959, **36**, 59
2. Storey, P. D., *Proc. 13th Int. Pyrotech. Semin.*, 1988, 765—784
3. Chapman, D. *et al., J. Pyrotech.*, 1998 (7), 51
4. Cardillo, P., *J. Loss Prevention Proc. Ind.*, 2001, **14**, 69

The chemistry involved in this explosively unstable system is reviewed [1]. The mechanism of the trigger reactions that initiate the exothermic decomposition of chlorate—sulfur mixtures has been studied. Mixtures containing 1—30% of sulfur can decompose well below the m.p. of sulfur, and addition of sulfur dioxide, the suspected chemical trigger, causes immediate onset of the reaction [2]. Autoignition of stoichiometric mixtures can be as low as 115°C, with frictional sensitivity at 5N, the lowest load the test apparatus permitted. Both were dependent upon the history of the sulphur used [3]. An account of historical explosions includes contemporary accounts of the fatal 18th century accidents resulting from the attempt to replace the nitrate in black powder by chlorate [4].

See Non-metals, above

Sulfur dioxide MRH 1.80/56

Mellor, 1947, Vol. 10, 217; 1941, Vol. 2, 311

Contact at temperatures above 60°C causes flashing of the evolved chlorine dioxide. Solutions of sulfur dioxide in ethanol or ether cause an explosion on contact at ambient temperature.

Sulfur, Metal derivatives

McKown, G. L. *et al., Chem. Abs.*, 1977, **87**, 103955

The sensitivity of chlorate—sulfur mixtures to initiation is increased by cobalt and its oxide, greatly so by copper nitride, copper sulfate, and extremely so by copper chlorate. Implications for manufacturing operations are discussed.

Sulfuric acid

1. Mellor, 1947, Vol. 10, 435
2. Bailar, 1973, Vol. 2, 1362

Addition of potassium chlorate in portions to sulfuric acid maintained at below 60 or above 200°C causes brisk effervescence. At intermediate temperatures, explosions are caused by the chlorine dioxide produced, and these reach maximum intensity at 120—130°C [1]. Uncontrolled contact of any chlorate with sulfuric acid may be explosive. The need for great caution with this system was stressed by Davy in 1815 [2].

See other METAL CHLORATES: Acids

Tannic acid

Rüst, 1948, 336

A mixture exploded during grinding in a mortar.

See other METAL CHLORATES

Thiourea

1. Soothill, D., *Safety Management*, 1992, **8**(6), 11.
2. Wharton, R. K. *et al., Propellants, Explos., Pyrotech.*, 1993, **18**(2), 77

An explosion is mentioned consequent upon grinding potasssium chlorate in equipment previously used for thiourea. It is claimed the mixture explodes spontaneously [1]. This is an exaggeration, it is very sensitive to friction, shock and heat (ignition <155°C) [2].

Thorium dicarbide

See Thorium dicarbide: Non-metals, etc.

See other METAL CHLORATES, OXIDANTS

4012. Potassium perchlorate

[7778-74-7] **$ClKO_4$**

$$K^+ \qquad O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{Cl}}{=}O$$

Aluminium powder, Titanium dioxide

Anon., *Fire Prot. Assoc. J.*, 1957, (36), 9

A mixture of the 3 compounds exploded violently during mixing. Previously the mixture had been accidentally ignited by a spark. Aluminium powder is incompatible with oxidants, and its mixture with titanium dioxide is a thermite-like combination.
See Aluminium: Metal oxides
See also THERMITE REACTIONS

Aluminium, Aluminium fluoride
1. Hahma, A., *Propellant, Explosives, Pyrotechnics*, 1996, 21, 100
2. Freeman, E. S. *et al., Combust. Flame*, 1966, **80**, 16

Whether mixtures of the perchlorate with aluminium truly detonate is under debate. However, appropriate compositions certainly explode violently even when uncontained, so the deflagration/detonation dispute is essentially academic [1]. Presence of aluminium fluoride increases the ease of ignition of aluminium—perchlorate mixtures, owing to complex fluoride formation [2].

Aluminium, Barium nitrate, Potassium nitrate, Water
See Aluminium: Metal nitrates, etc.

Barium chromate, Tungsten and/or Titanium
1. Carrazza, J. A. *et al., Chem. Abs.*, 1975, **82**, 113751
2. Nagaishi, T., *Chem. Abs.*, 1978, **88**, 173088

Mixtures containing 65% of tungsten with organic binders were developed as priming charges for surface flares [1]. Ignition of the dual metal—oxidant mixtures by IR irradiative heating was studied [2].
See other IRRADIATION DECOMPOSITION INCIDENTS

Boron, Magnesium, Silicone rubber
Paulin, C. J. *et al.*, US Pat, 4 101 352, 1978
Ignition of a compressed mixture, applied as a 6 mm layer on electronic components generates enough heat effectively to destroy them.

Combustible materials MRH Ethylene glycol 4.48/27
Grodzinski, J., *J. Appl. Chem.*, 1958, **8**, 523—528
Explosion temperatures were determined for a wide range of combustible liquid and solid organic materials sealed into glass tubes with potassium perchlorate. The lowest temperatures were shown by mixtures with ethylene glycol (240°), cotton linters (245°) and furfural (270°C).

Ethanol MRH 4.85/18
Burton, H. *et al., Analyst*, 1955, **80**, 16
Many explosions have been experienced during the gravimetric determination of either perchlorates or potassium as potassium perchlorate by a standard method involving an ethanol extraction. During subsequent heating, formation and explosion of ethyl perchlorate is very probable.

Ferrocenium diamminetetrakis(thiocyanato-*N*)chromate(1—)
Guslev, V. G. *et al., Chem. Abs.*, 1974, **86**, 57615

Presence of 25% of the organometallic salt (ferrocenium reineckate) considerably increases the rate of thermal decomposition of the perchlorate, involving hydrogen cyanide arising from the thiocyanato groups.

Lactose

See Lactose: Oxidants

Metal powders MRH MRH Aluminium 9.96/33, iron 3.76/51, magnesium 10.25/41, sodium 4.27/45

1. Schumacher, 1960, 210
2. Riffault, M. L., *Chem. Abs.*, 1975, **82**, 127130
3. Ywenkeng, H., *Chem. Abs.*, 1981, **94**, 194474
4. Rittenhouse, C. *et al., Proc. 6th Int. Pyrotech. Semin.*, 1978, 519—536
5. Wild, R. *J. Haz. Mat.*, 1982, **7**, 75—79
6. Munger, A. C. *et al., Chem. Abs.*, 1973, **98**, 91971
7. Parks, R. L., *Chem. Abs.*, 1981, **95**, 100052
8. Sarawadekar, R. G. *et al., Proc. 8th Int. Protech. Semin.*, 1982, 574—587

The mixture of aluminium and/or magnesium powders with potassium perchlorate (a photoflash composition) is very readily ignited and three industrial explosions have occurred. Mixtures of nickel and titanium powders with the oxidant and infusorial earth are very friction-sensitive, causing severe explosions, and easily ignited by very small (static) sparks [1]. A mixture containing 70% of molybdenum powder ignites at 330°C [2], and the rate of combustion of a mixture containing 48% is accelerated by 1% of various additives [3]. The pyrotechnic mixture with aluminium is insensitive to spark discharges but ignited consistently with a hot wire source [4], and blast waves produced on ignition of mixtures with 70% oxidant have been investigated [5]. The mixture with iron powder is sufficiently exothermic after ignition for use in metal welding, and an iron oxide—aluminium—nickel thermite mixture was also developed for the same purpose [6]. Data on detonation and deflagration of the pyrotechnic mixture with titanium were determined in open and closed vessels, and subsequently used to design a containment room for blending the powdered components [7]. The pyrotechnic/explosive perchlorate—tantalum system has been studied [8].

See Aluminium, etc., Boron, etc. and Barium chromate, etc., all above

See also THERMITE REACTIONS

See other FRICTIONAL INITIATION INCIDENTS, STATIC INITIATION INCIDENTS

Other reactants

Yoshida, 1980, 80

MRH values calculated for 18 combinations with oxidisable materials are given.

Potassium hexacyanocobaltate(3—)

Massis, T. M. *et al., Chem. Abs.*, 1977, **87**, 8142

Mixtures serve as gasless pyrotechnic compositions.

Reducants

See Metal powders, above; Titanium hydride, below

Sulfur MRH 3.39/20

Schumacher, 1960, 211—212

Mixtures of sulfur and potassium perchlorate, used in pyrotechnic devices, can be exploded by moderate impact. All other inorganic perchlorates form such impact-sensitive mixtures.

Titanium hydride

1. Massis, T. M. *et al., Rept. SAND-75-5889*, Richmond (Va.), USNTIS, 1976
2. Collins, L. W., *J. Haz. Mat.*, 1982, **5**, 325—333
3. Parks, R. L., *J. Haz. Mat.*, 1982, **5**, 359—371

The stability of the pyrotechnic mixture has been studied, including the effect of hydrogen content of the hydride [1]. Presence of moisture and impurities adversely affects stability [2], and remote handling facilities for the mixture have been developed [3].

See other METAL PERCHLORATES, OXIDANTS

4013. Potassium perchlorylamide

[15320-25-9] **ClK_2NO_3**

$$K^+ \qquad K^+ \qquad O{=}\overset{\overset{O}{\|}}{\underset{\underset{N^{2-}}{|}}{Cl}}{=}O$$

Sorbe, 1968, 67

Like the monopotassium salt, it will explode on impact or exposure to flame.

See entry PERCHLORYLAMIDE SALTS

See other N-METAL DERIVATIVES

4014. Lithium chlorite

[27505-49-3] **$ClLiO_2$**

Janz, 1976, Table 2, p. 10

It disproportionates violently on heating.

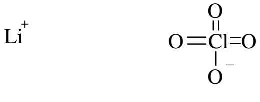
Chlorine, 2-Chloroalkyl aryl sulfides

See Chlorine: 2-Chloroalkyl aryl sulfides, etc.

See other CHLORITE SALTS, OXIDANTS

4015. Lithium perchlorate

[7791-03-9] **$ClLiO_4$**



$$Li^+ \qquad O{=}\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{Cl}}{=}O$$

Diethyl ether

1. Urben, P. G., *Chemtech*, 1991, (May), 259

2. Silva, R. A., *Chem. Eng. News*, 1992 **70**(51), 2
3. Handy, S. T. *et al., Synlett.*, 1995, 565
4. Long J.R., *Chem. Eng. News*, 2000, **78**(22), 16

A warning was given that the 5 molar solution in ether used as a solvent for Diels-Alder reactions would lead to explosions [1]. Such a reaction of dimethyl acetylenedicarboxylate and cyclooctatetraene in this solvent exploded very violently on heating. The cyclooctatetraene was blamed, with no supporting evidence [2]. It would appear desirable to find the detonability limits of any reaction mixture before any attempt is made to scale up. Initial studies have not shown detonability in any lithium perchlorate solution in an organic solvent, while adiabatic calorimetry showed exothermicity only above 150°C. Further testing is recommended [4]. A safe alternative to lithium perchlorate/ether as a solvent for Diels-Alder reactions is proposed [3].

See Dimethyl acetylenedicarboxylate, 1,3,3,7-Cyclooctatetraene
See Magnesium perchlorate

1,3-Dioxolane

Newman, G. H. *et al., J. Electrochem. Soc.*, 1980, **127**, 2025—2027

Lithium perchlorate—dioxolane electrolyte systems are unsafe for secondary battery applications, as an explosion occurred during overnight cyclic testing of a Li/TiS_2 system. The effect was duplicated under all over-discharge or cell-reversal conditions.

Hydrazine

Rosolovskii, V. Ya., *Chem,. Abs.*, 1969, **70**, 53524

Interaction gives only the dihydrazine complex, which explodes on grinding, but loses hydrazine uneventfully on heating at atmospheric or reduced pressure. The sodium salt is similar.

Nitromethane

See Nitromethane: Lithium perchlorate

Olefins, Electrophiles.

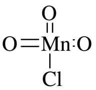
Zefirov, N. S., XIII Int. Symp. Org. Chem. Sulfur, 1988 (lecture; this information not in the later published proceedings).

Electrophilic additions to olefins, especially of XCl species, can give substantial quantities of perchlorate esters as by-products if performed in the presence of lithium perchlorate. These esters are extremely explosive, and may concentrate during distillation of crude products.

See other METAL PERCHLORATES, OXIDANTS

4016. Manganese chloride trioxide

[15605-27-3] **$ClMnO_3$**



$$O{=}\overset{\displaystyle O \atop \displaystyle \|}{\underset{\displaystyle | \atop \displaystyle Cl}{Mn}}{:}O$$

Briggs, S. T., *J. Inorg. Nucl. Chem.*, 1968, **30**, 2867—2868

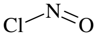
Explosively unstable if isolated as a liquid at ambient temperature, it may be handled safely in carbon tetrachloride solution.

See Manganese dichloride dioxide, Manganese trichloride oxide

See related METAL OXIDES

4017. Nitrosyl chloride

[2696-92-6] **ClNO**



It is a moderately endothermic compound (ΔH_f° (g) +52.6 kJ/mol, 0.80 kJ/g).

Acetone, Platinum

Kaufmann, G. B., *Chem. Eng. News*, 1957, **35**(43), 602

A cold sealed tube containing nitrosyl chloride, platinum wire and traces of acetone exploded violently on being allowed to warm up.

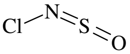
Hydrogen, Oxygen

See Nitrogen oxide: Hydrogen, etc.

See other ENDOTHERMIC COMPOUNDS, N-HALOGEN COMPOUNDS, NITROSO COMPOUNDS, OXIDANTS

4018. *N*-Chlorosulfinylimide

[25081-01-0] **ClNOS**



Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 318

The ampouled solid exploded violently on melting. Distillation at ambient pressure and impact tests had not previously indicated instability.

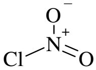
Chlorine fluoride

See Chlorine fluoride: *N*-Chlorosulfinylamine

See other N-HALOGEN COMPOUNDS, N—S COMPOUNDS

4019. Nitryl chloride

[13444-90-1] **ClNO$_2$**



It is feebly endothermic (ΔH_f° (g) +12.1 kJ/mol, 0.15 kJ/g) but a powerful oxidant gas.

Inorganic materials

Batey, H. H. *et al., J. Amer. Chem. Soc.*, 1952, **74**, 3408

Interaction of the chloride with ammonia or sulfur dioxide is very violent, even at — 75°C, and is vigorous with tin(II) bromide or tin(II) iodide.

Organic matter

Kaplan, R. *et al., Inorg. Synth.*, 1954, **4**, 54

It attacks organic matter rapidly, sometimes explosively.

B-Trimethylborazine

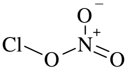
Hirata, T., *Rept, AD-7293939*, Richmond (Va.), USNTIS, 1971

Interaction is violent in absence of a diluent.

See other ENDOTHERMIC COMPOUNDS, N-HALOGEN COMPOUNDS, OXIDANTS

4020. Nitryl hypochlorite ('Chlorine nitrate')

[14545-72-3] **$ClNO_3$**



Metals, or Metal chlorides

Bailar, 1973, Vol. 2, 379

Interaction with most metals and metal chlorides is explosive at ambient temperature, but controllable at between —40 and —70°C.

Organic materials

Schmeisser, M., *Inorg. Synth.*, 1967, **9**, 129

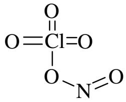
Not inherently explosive, but it reacts explosively with alcohols, ethers and most organic materials.

See Nitryl hypofluorite

See other HYPOHALITES, OXIDANTS

4021. Nitrosyl perchlorate

[15605-28-4] **$ClNO_5$**



Gerding, H. *et al., Chem. Weekbl.*, 1956, **52**, 282—283

Although stable at ambient temperature, it begins to decompose below 100°C, and at 115—120°C the decomposition becomes a low-order explosion.

Organic materials

Hofmann, K. A. *et al., Ber.*, 1909, **42**, 2031

As the anhydride of nitrous and perchloric acids, it is a very powerful oxidant. Pinene explodes sharply; acetone and ethanol ignite, then explode; ether evolves gas, then explodes after a few s delay. Small amounts of primary aromatic amines —aniline, toluidines, xylidines, mesidine— ignite on contact, while larger amounts exploded dangerously, probably owing to rapid formation of diazonium perchlorates. Urea ignites on stirring with the perchlorate, (probably for a similar reason).

See other NON-METAL PERCHLORATES, OXIDANTS

Pentaammineazidocobalt(III) perchlorate, Phenyl isocyanate

Burmeister, J. L. *et al., Chem. Eng. News*, 1968, **46**(8), 39

During an attempt to introduce phenyl isocyanate into the Co coordination sphere, a mixture of the 3 components exploded violently when stirring was stopped.

4022. Nitronium perchlorate

[12051-08-0] **$ClNO_6$**

Albright, Hanson, 1976, 2

The explosively unstable behaviour of stored nitronium perchlorate is attributed to the formation of small equilibrium concentrations of the isomeric covalent nitryl perchlorate ester (below).

1,2-Epoxides

Golding, P. *et al., Tetrahedron Lett.*, 1988, **29**, 2733

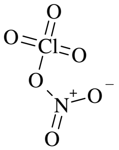
Reaction with epoxides gives the dangerously unstable and explosive mixed nitrate—perchlorate diesters, such as 1,2-ethanediyl nitrate perchlorate from ethylene oxide.

See other NON-METAL PERCHLORATES

See related NITRATION INCIDENTS

4023. Nitryl perchlorate

[17495-81-7] **$ClNO_6$**



Ammonium perchlorate

See Ammonium perchlorate: Impurities

Organic solvents

1. Spinks, J. W. T., *Chem. Eng. News*, 1960, **38**(15), 5
2. Gordon, W. E. *et al., Can. J. Res.*, 1940, **18B**, 358

Interaction with benzene gave a slight explosion and flash [1], while sharp explosions with ignition were observed with acetone and ether [2].

See other NON-METAL PERCHLORATES, OXIDANTS

4024. Chlorine azide

[13973-88-1] **ClN_3**

$N\overset{-}{=}N\overset{+}{=}N-Cl$

Alone, or Ammonia, or Phosphorus, or Silver azide, or Sodium

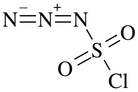
1. Frierson, W. J. *et al., J. Amer. Chem. Soc.*, 1943, **65**, 1696, 1698
2. Rice, W. J. *et al., J. Chem. Educ.*, 1971, **48**, 659
3. Combourieu, J. *et al., Chem. Abs.*, 1977, **87**, 123313
4. Tornieporth-Oetting, I. C. *et al., Angewand. Chem. (Int.),* 1995, **34**(5), 511

The undiluted material is extremely unstable, usually exploding violently without cause at any temperature, even as solid at —100°C [1]. Explosion is likely to be triggered by pressure fluctuations of around 10 Pa [4]. It gives an explosive yellow liquid with liquid ammonia; when condensed on to yellow phophorus at —78°C an extremely violent explosion soon occurs. Addition of phosphorus to a solution of the azide in carbon tetrachloride at 0°C causes a series of mild explosions if the mixture is stirred, or a violent explosion without stirring. Contact of the liquid or gaseous azide with silver azide at —78°C gave a blue colour, soon followed by explosion, and sodium reacted similarly under the same conditions [1]. When chlorine azide (25 mol %) is used as a thermally activated explosive initiator in a chemical gas laser tube, the partial pressure of azide should never exceed 16 mbar [2]. The explosive decomposition has been studied in detail [3].

See entry HALOGEN AZIDES

4025. Sulfuryl azide chloride

[13449-15-5] **ClN_3O_2S**



Preparative hazard

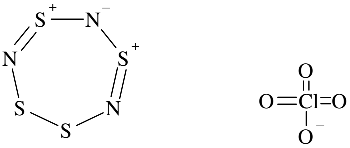
Shozda, R. J. *et al., J. Org. Chem.*, 1967, **32**, 2876

During the preparation of this explosive liquid by interaction of sulfuryl chloride fluoride and sodium azide, traces of chlorine must be eliminated from the former to avoid detonation. The product is nearly as shock-sensitive as glyceryl nitrate and may explode on rapid heating. Solutions (25 wt%) in solvents may be handled safely. The corresponding fluoride is believed to behave similarly.

See other ACYL AZIDES, ACYL HALIDES, NON-METAL AZIDES

4026. Thiotrithiazyl perchlorate

[ ] **$ClN_3O_4S_4$**



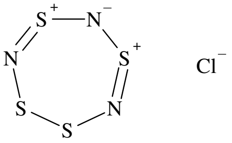
Organic solvents

Goehring, 1957, 74

The precipitated perchlorate salt exploded on washing with acetone or ether.

See other NON-METAL PERCHLORATES, N—S COMPOUNDS

4027. Thiotrithiazyl chloride
[12015-30-4] **ClN_3S_4**



Alone, or Ammonia

1. Mellor, 1940, Vol. 8, 631—632
2. Bailar, 1973, Vol. 2, 903

The dry chloride, which explodes on heating in air, will rapidly absorb ammonia gas and then explode [1]. The structure of the cation is now known to be a 7-membered ring with only 2 adjacent sulfur atoms. Thiotrithiazyl salts other than the chloride are also explosive [2].

See Thiotrithiazyl nitrate, Thiotrithiazyl perchlorate

See other NON-METAL HALIDES, N—S COMPOUNDS

4028. Cyclopentaazathienium chloride
[88433-73-2] **ClN_5S_5**

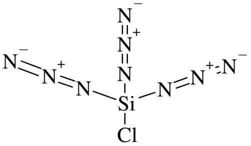
$$N_5S_5^+ \ Cl^-$$

Banister, A. J. *et al., J. Chem. Soc., Chem. Comm.*, 1983, 1017

It detonates on percussion and decomposes rapidly above 90°C to give a residue, largely thiotrithiazyl chloride, which explodes above 170°C.

See other N—S COMPOUNDS

4029. Triazidochlorosilane
[67880-25-5] **ClN_9Si**



It detonates on percussion and decomposes rapidly above 90°C to give a residue, largely thiotrithiazyl chloride, which explodes above 170°C.

See Silicon tetraazide

See other NON-METAL AZIDES, N—S COMPOUNDS

4030. Sodium chloride

[7647-14-5] **ClNa**

$Na^+ \quad Cl^-$

HCS 1980, 834

Vainshtein, D. *et al., Chem. Abs.*, 2000, **132**, 354662k
Heavily irradiated salt accumulates energy up to 1.4 kJ/g which may be released explosively. This is presumably mostly physical (Wigner distortion), but dissociation to the elements may contribute.
See other IRRADIATION DECOMPOSITION INCIDENTS

Dichloromaleic anhydride, Urea
See Dichloromaleic anhydride: Sodium chloride, etc.

Lithium
See Lithium: Sodium carbonate, etc.

Nitrogen compounds
Rosinski, M. *et al., Chem. Abs.*, 1980, **93**, 15512
Electrolysis of sodium chloride in presence of nitrogenous compounds to produce chlorine may lead to formation of explosive nitrogen trichloride. Precautions are detailed.

Water
Aleshin, G. Ya., *Chem. Abs.*, 1982, **96**, 220112
The mechanism of explosion of molten salt at 1100°C in accidental contact with water was studied.
See MOLTEN SALTS
See other METAL HALIDES

4031. Sodium hypochlorite

[7681-52-9] **ClNaO**

$Na^+ \quad O^{-}\text{-}Cl$

FPA H52, 1976; *HCS 1980*, 213, 847, 848 (5, 10, 15% solns, resp.)

1. Brauer, 1963, Vol. 1, 311
2. Sorbe, 1968, 85

The anhydrous solid obtained by desiccation of the pentahydrate will decompose violently on heating or friction [1,2].

Amines — MRH Aniline 3.10/26
Kirk-Othmer, 1963, Vol. 2, 105
Primary aliphatic or aromatic amines react with sodium hypochlorite (or calcium hypochlorite) to form *N*-mono- or di-chloroamines which are explosively unstable, but less so than nitrogen trichloride.

Ammonium salts

1. Anon., *Loss Prev. Bull.*, 1978, (022), 116
2. Anon., *Occ. Safety Health*, 1976, **6**(4), 2
3. Anon., *Sichere Chemiearbeit*, 1996, **48**(10), 114

Contact in the drains of an effluent containing the hypochlorite with one containing ammonium salts and acid led to formation of nitrogen trichloride which decomposed explosively. The effect was reproduced under laboratory conditions [1]. Cleaning a brewery tank with an acidified ammonium sulfate cleaning preparation, then sodium hypochlorite solution without intermediate rinsing, led to nitrogen trichloride formation and a violent explosion [2]. The reservoir of a scrubber system whch had previously been employed to scrub ammonia containing off-gas with dilute acid was charged with sodium hypochlorite solution for another process. There was a violent explosion, destroying the reservoir and scrubber assembly. Investigation showed that the reservoir had not been fully cleaned from the previous operation [3].
See Amines, above; Phenylacetonitrile, below

Aziridine

Graefe, A. F. *et al., J. Amer. Chem. Soc.*, 1958, **80**, 3839
Interaction of ethyleneimine with sodium (or other) hypochlorite gives the explosive *N*-chloro compound.
See 1-Chloroaziridine

Carbonised residue

Dokter, T., *J. Haz. Mat.*, 1985, **10**, 85
A saucepan of vegetable stew had been heated too long and had formed a thick carbonised adherent cake. In an attempt to clean the pan, 1 l of domestic bleach was added and the pan was left to heat on an electric hotplate. Again it was left too long and after all the water had evaporated, the residue exploded violently. This was attributed to formation of sodium chlorate during evaporation, and ignition of the overheated chlorate-impregnated carbonised mass.
See Sodium chlorate: Organic matter

Ethanediol

Bickerton, J., *Chem. Brit.*, 1991, **27**(6), 504
Mixtures of aqueous sodium hypochlorite (presumably the 15% available chlorine commercial product) and ethylene glycol were observed to erupt violently after an induction period of 4 to 8 minutes. Caution is advised in view of the use of glycol as a cooling fluid in industrial reactors.

Formic acid

Khristoskova, S., *Chem. Abs.*, 1983, **98**, 95125
Removal of formic acid from industrial waste streams with sodium hypochlorite solution becomes explosive at 55°C.
See other REDOX REACTIONS

Furfuraldehyde

Birchwood, P. J., *Chem. Brit.*, 1985, **21**, 29

In a variation of the usual reaction conditions for oxidising furfuraldehyde to 2-furoic acid with hypochlorite, the aldehyde was added dropwise to a 10% excess of commercial sodium hypochlorite solution at 20—25°C, but without the inclusion of additional sodium hydroxide. When aldehyde addition was almost complete, a violent explosion occurred. Subsequent investigation showed that the pH of the reaction mixture fell progressively with addition of aldehyde, and at pH 8.5 the reaction mixture erupted violently, the temperature increased by 70°C and the pH fell to 2. Similar results were seen with benzaldehyde, but not with thiophene-2-aldehyde.

'Imidate'

Rayner, P., *Safety Digest Univ. Safety Assoc.*, 1991, **40**, 14

A methyl but-3-enylimidate ester hydrochloride, was charged to a tenfold excess of stirred 14% hypochlorite solution cooled in ice. After 50 min the flask was removed to replenish the ice. Shortly after returning the flask to the icebath a violent explosion shattered both flask and icebath. This was attributed to thermal runaway (although available energy is scarcely sufficient to boil the water in the flask). It seems more likely that trichloroamine was generated by the excess hypochlorite, settled when removed from the magnetic stirrer, and detonated from friction when this restarted. The reaction is said to have been performed many times previously without incident.

See Nitrogen trichloride

See other AGITATION INCIDENTS

Methanol MRH 2.47/10

ICI Mond Div., private comm., 1968

Several explosions involving methanol and sodium hypochlorite were attributed to formation of methyl hypochlorite, especially in presence of acids or other esterification catalyst.

Other reactants

Yoshida, 1980, 132

MRH values calculated for 17 combinations with oxidisable materials are given.

Phenylacetonitrile

Libman, D. D., private comm., 1968

Use of sodium hypochlorite solution to destroy acidifed benzyl cyanide residues caused a violent explosion, thought to have been due to formation of nitrogen trichloride.

Photographic developer

Anon., *Environment, Safety & Health Bull.*, 1993, **93**(2), 1

As part of an analytical procedure prior to silver recovery, 10 ml commercial hypochlorite solution (15% available chlorine?) was added to highly alkaline waste developer solution. The redox reaction was violent enough to spray the worker, causing alkali burns.

Sodium ethylenediaminetetracetate, Sodium hydroxide

Schierwater, F.-W., *Sichere Chemiearb.*, 1987, **39**, 35

Operating instructions specified that 50% sodium hydroxide solution, sodium hypochlorite solution and sodium EDTA solution were to be added separately by pumping

into an off-gas scrubber unit, when the exotherms would be dissipated slowly in the solution tank. An attempt to simplify the operation by premixing the 3 solutions in a drum before pumping the mixture, led to vigorous foaming decomposition. Mixing the conc. alkali with the bleach caused the oxidant to become heated by the heat of dilution of the former, and oxidation of the EDTA component then proceeded exothermically with decomposition (and evolution of carbon dioxide).
See other GAS EVOLUTION INCIDENTS

Sodium metabisulfite

1. www.chemsafety.gov/circ., US Chem. Safety Board Incident No. 2002-5486
2. Editor's comment

A garbled report indicates that on one of many occasions when a cleaning solution was mixed from these salts and sodium hydroxide, there was a runaway evolving chlorine [1]. What limited stability this mixture of an acid unstable oxidant and a weakly acidic reducant can have will only be imparted by the sodium hydroxide, one suspects that it may have been to be charged as listed; last [2].

Water

Hazard Note HN(76)189, Dept. of Health and Social Security, London, 1976
Two 2.5 l bottles of strong sodium hypochlorite solution (10—14% available chlorine) burst in storage, owing to failure of the cap designed to vent oxygen slowly evolved during storage. This normal tendency may have been accelerated by the unusually hot summer. Vent caps should be checked with full personal protection, and material should be stored at 15—18°C and out of direct sunlight, which accelerates decomposition.
See other METAL HYPOCHLORITES

4032. Sodium chlorite

[7758-19-2] **$ClNaO_2$**

FPA H109, 1972; *HCS 1980*, 835

1. Brauer, 1963, Vol. 1, 312
2. Leleu, *Cahiers*, 1974, (74), 137
3. Mellor, 1956, Vol. 2 (Suppl. II, Pt. 1), 573
4. Ullmann, 1986, A6, 500
5. Simoyi, R. H. *et al., Chem. Eng. News*, 1993, **71**(12), 4
6. www.chemsafety. gov/circ, U.S. Chemical Safety and Hazard Investigation Board, CSB 2000-4765
7. Jasiewicz, M., *Chem. & Ind.* 1999, 202

The anhydrous salt explodes on impact [1], and decomposes violently at 200°C [2]. The trihydrate is also percussion sensitive [3] though other sources suggest that in clean, grease- and oil-free equipment the anhydrous salt is shockproof [4]. A bottle of the purified anhydrous salt exploded then 'burnt' on opening, (transition to sodium chloride and oxygen has an enthalpy of 1.2 kJ/g), presumably initiated by friction in the screw cap (most screw caps are combustible). Various contaminants, including iron and ammonium salts, may sensitise sodium chlorite [5]. A fire was started when the cap was screwed onto a plastic tube containing sodium chlorite [6]. A largely empty polythene sack of sodium chlorite (2 kg remaining) deflagrated during removal of portions with a plastic scoop. The scoop and sack will have provided considerable fuel to an oxidant capable of deflagrating without such assistance. Ignition may have been by static discharge [7].

Acids MRH Several inorganic acids, all 1.17/tr.

Bailar, 1973, Vol. 2, 1413

Under normal conditions, solutions of sodium (and other) chlorites when acidified do not evolve chlorine dioxide in dangerous amounts. However, explosive concentrations may result if acid is dropped onto solid chlorites.

See Oxalic acid, below

Carbon MRH 3.60/9

Leleu, *Cahiers*, 1980, (99), 278

A mixture with powdered charcoal ignited above 60°C.

Ethylene glycol MRH 3.51/17

See Ethylene glycol: Oxidants

Oils MRH Octane 4.60/22, toluene 4.35/33

Karzhenyak, I. G. *et al., Chem. Abs.*, 1981, **95**, 67122

In presence of oils, the chlorite is friction- and shock-sensitive.

Organic matter MRH Cellulose 3.76/24

The Diox Process, Newark, N.J., Wallace and Tiernan, 1949

Intimate mixtures of the solid chlorite with finely divided or fibrous organic matter may be explosive and very sensitive to heat, impact or friction.

Other reactants

Yoshida, 1980, 4—7

MRH Values calculated for no fewer than 79 combinations, largely with oxidisable materials, are given.

Oxalic acid

1. *MCA Case History No. 839*
2. Stull, 1977, 20

A bleach solution was being prepared by mixing solid sodium chlorite, oxalic acid, and water, in that order. As soon as water was added, chlorine dioxide was evolved and later exploded. The lower explosive limit of the latter is 10%, and the mixture is photo- and heat-sensitive [1]. It was calculated that the heat of reaction (1.88 kJ/g of dry mixture) would heat the expected products to an adiabatic temperature approaching 1500°C with an 18-fold increase in pressure in a closed vessel [2].

Phosphorus MRH (Yellow) 6.23/21

Mellor, 1971, Vol. 8, Suppl. 2.2, 645

Red phosphorus and the chlorite react very exothermally in aqueous suspension above 50°C, and there may be a sudden and near-explosive stage in the redox reaction after an induction period.
See other INDUCTION PERIOD INCIDENTS, REDOX REACTIONS

Photographic developer
Usher, J. www.dne.bnl.gov/etd/csc/1992 (quarter 3)
While attempting silver recovery from spent developer, a commercial preparation, described as sodium chlorite, was added to the developer, causing violent reaction and spraying the experimenter. There is a suggestion that ammonia was present, and sodium hydroxide, despite which it is claimed that hydrochloric acid was part of the gas release. Poor mixing was involved. Developers being reducants, no involvement of the other destabilising materials (silver, ammonia) need be assumed.

Sodium dithionite
Anon., *Chem. Trade J.*, 1953, **132**, 564
Use of a scoop contaminated with sodium dithionite for sodium chlorite caused ignition of the latter. Materials containing sulfur (dithionite, natural rubber gloves) cause decomposition of sodium chlorite and contact should be avoided.

Sulfur-containing materials MRH Sulfur 3.64/15, diethyl sulfide 4.27/28
1. Leleu, *Cahiers*, 1974, (74), 138
2. Weber, J. U. *et al., Rec. Trav. Chim.*, 1986, **105**(3), 99—102

Sodium chlorite reacts very violently with organic compounds of divalent sulfur, or with free sulfur (which may ignite), even in presence of water. Contact of the chlorite with rubber vulcanised with sulfur or a divalent sulfur compound should therefore be avoided [1]. Application of factorial design techniques to experimental planning gave specific conditions for the safe oxidation of organic sulfides to sulfoxides using sodium chlorite or calcium hypochlorite [2].
See Sodium dithionite, above

Zinc MRH 3.60/58
Karzhenyak, I. G. *et al., Chem. Abs.*, 1981, **95**, 64606
Mixtures containing less than 0.1% of zinc dust or other assorted technical materials are not explosive or combustible on impact or friction.
See other CHLORITE SALTS, METAL OXOHALOGENATES, OXIDANTS

4033. Sodium chlorate
[7775-09-9] **$ClNaO_3$**

(*MCA SD-52*, 1952); *FPA H7*, 1972; *HCS 1980*, 833

1. *The Fire and Explosion at Braehead Container Depot, Renfrew, 1977*, London, HMSO, 1979
2. *The Fire and Explosion at River Road, Barking, Essex, 1980*, London, HSE, 1980

3. *Anon., New Scientist*, 1982, 595 (1325), 892
4. U.S. National Transportation Safety Board, 1997, Aircraft Accident Report 6704B

Following a violent explosion during a fire involving 67 t of drummed sodium chlorate, experiments confirmed that pure sodium chlorate would decompose explosively under intense fire conditions. An appended report by HM Inspector of Explosives detailed six incidents since 1899 involving explosions during fires in stores holding potassium or sodium chlorate [1]. A later incident involving explosive thermal decomposition of 2.5 t of the salt led to a drastic downward revision of the minimum quantity thought to pose this hazard [2]. A third incident in 1982 again involved explosion of drums of sodium chlorate in a warehouse fire [3]. It is difficult to understand this apparent reluctance to gain benefit from the recorded experience of over 80 years.

Emergency oxygen generators for passenger aircraft operate by deflagration of sodium chlorate lightly doped with barium peroxide and potassium perchlorate. Such units, carried in bulk as cargo and triggered by accident, giving hotspots of at least 250°C in an oxygen enriched atmosphere, have been involved in aircraft mishaps, at worst causing a crash killing 110 passengers. Safety devices preventing initiation are removed on installation. The generators, time expired by bureaupratic definition, but still entirely functional, may later be returned for refurbishing without these safety devices being replaced [4].

See Potassium chlorate

Agricultural materials

Reimer, B. *et al., Chem. Technik*, 1974, **26**, 447—447 (condensed paper)

The potential for explosive combustion of mixture of sodium chlorate-based herbicides with other combustible agricultural materials was determined. Initiation temperatures and maximum combustion temperatures were measured for mixtures of sodium (or potassium) chlorate with peat, powdered sulfur, sawdust, urotropine (hexamethylenetetramine), thiuram and other formulated materials. With many combinations, maximum temperature increases of 500—1000°C at rates of 400—1200°/s were recorded for 2 g samples.

Alkenes, Potassium osmate

Lloyd, W. D. *et al., Synthesis*, 1972, 610

The hydroxylation of alkenes to diols with potassium osmate—oxidant mixtures has been described, with either hydrogen peroxide or sodium chlorate as the oxidant. The sodium chlorate method is not applicable where the diol is to be distilled from the mixture, because of the danger of explosive oxidation of the product diol by the chlorate.

Aluminium, Rubber

Olson, C. M., *J. Electrochem. Soc.*, 1949, **116**, 34C

The rubber belt of a bucket elevator, fitted with aluminium buckets and used for transporting solid chlorate, jammed during use. Friction from the rotating drive pulley heated and powdered the jammed belt. A violent explosion consumed all the rubber belt and most of the 90 aluminium buckets. Bronze and steel equipment is now installed.

Ammonium salts, or Metals, or Non-metals, or Sulfides MRH values below references

1. *MCA SD-42, 1952*
2. *MCA Case History No. 2019*

MRH Aluminium 10.71/33, iron 4.35/50, magnesium 10.88/40, manganese 5.06/50, sodium 5.56/55, phosphorus 7.32/25, sulfur 4.27/20

Mixtures of the chlorate with ammonium salts, powdered metals, phosphorus, silicon, sulfur or sulfides are readily ignited and potentially explosive [1]. Residues of ammonium thiosulfate in a bulk road tanker contaminated the consignment of dry sodium chlorate subsequently loaded, and exothermic reaction occurred with gas evolution during several hours. Laboratory tests showed that such a mixture could be made to decompose explosively. A reaction mechanism is suggested.

See other GAS EVOLUTION INCIDENTS

Arsenic trioxide

Ellern, 1968, 51

Ignition may occur on contact.

1,3-Bis(trichloromethyl)benzene

See 1,3-Bis(trichloromethyl)benzene: Oxidants

Cyanides

See METAL CYANIDES (reference 1)

Cyanoborane oligomer

Gyori, B. *et al., J. Organomet. Chem.*, 1984, **262**(1), C7

A mixture exploded violently on mild mechanical agitation.

Diols

See Alkenes, etc., above

Grease

Olson, C. M., *J. Electrochem. Soc.*, 1969, **116**, 34C

The greased bearing of a small grinder exposed to chlorate dust exploded violently during cleaning. Fluorocarbon-based greases and armoured bearings are recommended for chlorate service, with full operator protection during cleaning operations.

See Organic matter, below

See also Sodium bromate: Grease

Leather

MCA Case History No. 1979

Shoes became contaminated with a chlorate weed-killer solution which dried out in wear. A welding spark later fell into the shoe and the front was blown off.

Nitrobenzene MRH 4.94/88

Hodgson, J. F., private comm., 1973

The combination is powerfully explosive and has been widely used in terrorist activities.

Organic matter MRH Carbon 4.73/12

1. *MCA SD-42*, 1952
2. Cook, W. H., *Can. J. Res.*, 1933, **8**, 509
3. Biasutti, 1981, 30
4. Anon., *Chem. Haz. in Ind.*, 1987, (7), item 1688
5. Anon., *Chem. Haz. in Ind.*, 1987, (10), item 2666

Mixtures of sodium (or other) chlorate with fibrous or absorbent organic materials (charcoal, flour, shellac, sawdust, sugar) are hazardous. If the chlorate concentration is high, the mixtures may be ignited or caused to explode by static sparks, friction or shock [1]. Even at 10—15% concentration, low relative humidity may allow easy ignition and rapid combustion to occur [2]. A fire originating thus led to destruction of part of an explosives factory [3]. Sparks from a grinder ignited newly-cleaned overalls, which had previously been contaminated with sodium chlorate [4]. It was later confirmed that the overalls had been dry-cleaned in perchloroethylene with added water, rather than being laundered in hot water. The latter cleaning method would have removed completely the sodium chlorate, which is soluble in water but not in halogenated solvents [5].

See Paper and Wood below

See also OXIDANTS AS HERBICIDES

See other FRICTIONAL INITIATION INCIDENTS, STATIC INITIATION INCIDENTS

Osmium

Rogers, D. B. *et al., Inorg. Synth.*, 1972, **13**, 141

During the preparation of osmium dioxide, the ampoule containing the reaction mixture must be cooled during sealing operations to prevent violent reaction occurring. Subsequent heating, first to 300 and then 600°C must also be effected slowly.

Other reactants

Yoshida, 1980, 70—71

MRH values calculated for 33 combinations with oxidisable materials are given.

Paint, Polythene

Lamb, J. A., *Chem. Brit.*, 1979, **15**, 125—126

A violent explosion occurred when the lid was levered off an old paint tin used to contain a polythene bag of sodium chlorate. Subsequent tests showed that low energy input (0.2 J) would cause explosion of unconfined chlorate on a rusty steel surface. The presence of contaminants (sawdust, copper acetate, paint flakes or shredded polythene) increases the sensitivity, and a mixture with paint flakes and polythene caused 100 mg portions to explode under 0.2 J impact in 24 out of 100 attempts.

Paper, Static electricity

1. Ewing, O. R., *Chem. Eng. News*, 1952, **30**, 3210
2. Grimmett, R. E. R., *New Zealand J. Agric.*, 1938, **57**, 224—225
3. Biasutti, 1981, 92

Paper impregnated with sodium chlorate and dried can be ignited by static sparks, but not by friction or impact. Paper bags or card cartons are unsuitable packing materials [1]. A previous incident involving paper sacks which had formerly contained mixed sodium and calcium chlorates had been noted [2]. The tendency of sodium chlorate to deliquesce or effloresce, depending on atmospheric temperature and humidity may lead, if the solid is packed in pervious containers, to the appearance of very fine crystals on the outside of a paper bag or cardboard box, etc. These fine crystals of high specific surface area are very sensitive to friction and initiation of ignition [3].

See other FRICTIONAL INITIATION INCIDENTS, STATIC INITIATION INCIDENTS

Phosphorus MRH (Yellow) 7.32/25

Anon., *Angew. Chem. (Nachr.)*, 1957, **5,** 78

A mixture of red phosphorus and sodium chlorate exploded violently.

Preparative hazard

Kirk-Othmer, 1994, 4th Edn., **9**, 153

There is a risk of generating hydrogen/chlorine/oxygen mixtures during electrolytic preparation from brine. An explosive limits diagram for this ternary system is given.

Sodium phosphinate MRH 2.89/55

See Sodium phosphinate: Oxidants

Sulfuric acid MRH 1.30/tr.

1. Anon., *ABCM Quart. Safety Summ.*, 1944, **15**, 3
2. *MCA Case History No. 282*

Erroneous addition of conc. sulfuric acid to sodium chlorate instead of sodium chloride caused an explosion owing to formation of chlorine dioxide [1]. Accidental contact of 93% acid on clothing previously splashed with sodium chlorate caused immediate ignition [2].

Titanium

See Titanium: Oxidants
Titanium: Sodium chlorate, etc.

Triethylene glycol, Wood

Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 112

A wooden pallet which ignited and burned fiercely was found to be contaminated with both the glycol and sodium chlorate to a level of 27%.

Wood

1. Anon., *ABCM Quart. Safety Summ.*, 1947, **18**, 25
2. Anon., *BCISC Quart. Safety Summ.*, 1967, **38**, 42
3. Kletz, T. A., *J. Loss Prev.Proc.Ind.*, 1989, **2**, 117

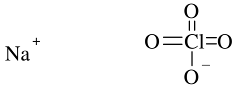
Various fires and explosions caused by use of wooden containers with chlorates, and precautions necessary during handling and storage, are discussed [1,2]. A wooden pallet burst into flames as it was dragged across ground contaminated with sodium chlorate [3].

See Organic matter, above

See other FRICTIONAL INITIATION INCIDENTS, METAL CHLORATES, OXIDANTS

4034. Sodium perchlorate

[7601-89-0] **$ClNaO_4$**



Hydrazine

Rosolovskii, V. Ya., *Chem. Abs.*, 1969, **70**, 53524

Interaction gives only a 1:1 complex which explodes on grinding, but dissociates uneventfully on heating at atmospheric or reduced pressure. The lithium salt is similar.

Other reactants

Yoshida, 1980, 82

MRH values calculated for 18 combinations with oxidisable materials are given.

Water

Moureu, H. *et al., Chem. Abs.*, 1951, **45**, 5929h

During concentration of an aqueous solution, an explosion occurred. Involvement of an unsuspected impurity seems probable.

Water-soluble fuels MRH values below reference

Annikov, V. E. *et al., Chem. Abs.*, 1983, **99**, 73190

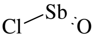
MRH Acetone 4.89/18, ethanol 4.73/18, ethylene glycol 4.35/26

The detonation and combustion limits of mixtures of sodium perchlorate, water and ethylene glycol, glycerol, 1,3-butylene glycol, 2,3-butylene glycol, formamide, dimethylformamide, ethanolamine, diaminoethane, acetone, urea and galactose have been studied.

See other METAL PERCHLORATES, OXIDANTS

4035. Antimony(III) chloride oxide

[7791-08-4] **ClOSb**



Bromine trifluoride

See Bromine trifluoride: Antimony(III) chloride oxide

See related METAL HALIDES, METAL OXIDES

4036. Chlorine dioxide

[10049-04-4] **ClO_2**

$O{=}Cl{=}O$

HCS 1980, 289

1. Sidgwick, 1950, 1203
2. Mellor, 1941, Vol. 2, 288

3. Stedman, R. F., *Chem. Eng. News*, 1951, **29**, 5030
4. Cameron, A. E., *Chem. Eng. News*, 1951, **29**, 3196
5. Fawcett, H. H., *Chem. Eng. News*, 1951, **29**, 4459
6. McHale, E. T. *et al., J. Phys. Chem.*, 1968, **72**, 1849
7. Jansen, M., *et al., Angew. Chemie (Int.)*, 1991, **30**(11), 1510
8. *Hazards of Chlorine Dioxide*, New York, Natl. Board of Fire Underwriters, 1950; *Chem. Eng. News*, 1950, **28**, 611
9. Derby, R. I. *et al., Inorg. Synth.*, 1954, **4**, 152
10. Bielz, S., Ger. Offen. 2 917 132, 1980
11. Cowley, G., *Loss Prev. Bull.*, 1993, (113), 1
12. Croce, A. *et al., Z. Phys. Chem. (Munich)*, 2000, **214**(4), 533
13. Simpson, G. D. *et al., Ind. Water Treat.*, 1995, **27**(5), 48
14. Ferweda, G., *Pulp & Paper*, 2004, **78**(6), 54

Chlorine dioxide is considerably endothermic (ΔH_f° (g) +103.3 kJ/mol, 1.53 kJ/g) and of limited stability. It is a powerful oxidant and explodes violently on the slightest provocation as gas or liquid [1]. It is initiated by contact with several materials (below), on heating rapidly to 100°C or on sparking [2], or by impact as solid at —100°C [3]. A small sample exploded during vacuum distillation at below —50°C [4], and it was stated that decomposition by sparking begins to become hazardous at concentrations of 7—8% in air [3], and that at 10% concentration in air (0.1 bar partial pressure) explosion may occur from any source of initiation energy, such as sunlight, heat or electrostatic discharge [5]. A kinetic study of the decomposition shows that it is explosive above 45°C even in absence of light, and subject to long induction periods due to formation of intermediate dichlorine trioxide. UV irradiation greatly sensitises the dioxide to explosion [6]. The solid (A dimer) can be relatively safely handled below —40°C and the gas at pressures below 50 mbar [7]. A guide on fire and explosion hazards in industrial use of chlorine dioxide is available [8], and preparative precautions have been detailed [9]. An improved and safer method for continuous production of chlorine dioxide is claimed [10]. A thorough review has been written, detailing numerous incidents, of hazards attending industrial preparation and use of chlorine dioxide (now much used as a low chlorine bleach). Liquid ClO_2 can separate from aqueous solutions > 60 g/l, it is exceedingly shock sensitive. A partial pressure of 130 mbar in air is thought entirely safe, as are aqueous solutions (but not necessarily the head space above them) [11]. Variations in explosive limit in air against pressure and temperature are studied [12]. The safe use of chlorine dioxide and sodium chlorite has been reviewed [13]. Safe industrial storage procedures are described [14].
See other ENDOTHERMIC COMPOUNDS, IRRADIATION DECOMPOSITION INCIDENTS, STATIC INITIATION INCIDENTS

Carbon monoxide MRH 5.35/45
Mellor, 1941, Vol. 2, 288
Explosion on mixing.

Fluoramines
Lawless, 1968, 171
Interaction with difluoramine or trifluoramine in the gas phase is explosive.

Hydrocarbons MRH Hexane, 6.61/12, Toluene 6.65/13

Leleu, *Cahiers*, 1979, (95), 297

Mixtures with butadiene, ethane, ethylene, methane or propane always explode spontaneously.

Hydrogen

Mellor, 1941, Vol. 2, 288

Near-stoicheiometric mixtures detonate on sparking, or on contact with platinum sponge.

Mercury

Mellor, 1941, Vol. 2, 288

The gas explodes on shaking with mercury.

Non-metals

Mellor 1941, Vol. 2, 289; 1956, Vol. 2, Suppl. 1, 532

Phosphorus, sulfur, sugar or combustible materials ignite on contact and may cause explosion.

Other reactants

Yoshida, 1980, 268

MRH values calculated for 19 combinations, largely with oxidisable materials, are given.

Phosphorus pentachloride MRH 1.55/71

See Phosphorus pentachloride: Chlorine dioxide

Potassium hydroxide MRH 1.92/37

Mellor, 1941, Vol. 2, 289

The liquid or gaseous oxide will explode in contact with solid potassium hydroxide or its conc. solution.

Sodium nitrite, Acid

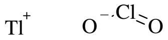
Briggs, T. S., *J. Chem. Educ.*, 1991, **68**(11), 938

An experiment is described which purports to show the detonation of a mixture of chlorine dioxide (described as a stable gas!) and nitric oxide formed from the above reagents. It seems likely it demonstrates detonation of chlorine dioxide, itself, initiated by either the nitrite or nitric oxide.

See other HALOGEN OXIDES, OXIDANTS

4037. Thallium(I) chlorite

[40898-91-7] **ClO_2Tl**

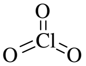


Bailar, 1973, Vol. 1, 1167

It is detonable by shock.

See other CHLORITE SALTS, HEAVY METAL DERIVATIVES

4038. Chlorine trioxide
[13932-10-0] **ClO_3**



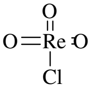
Schmeisser, M., *Angew. Chem.*, 1955, **67**, 498

The dimeric form is formulated as chloryl perchlorate.

See Chloryl perchlorate

See other HALOGEN OXIDES

4039. Rhenium chloride trioxide (Perrhenyl chloride)
[42246-25-3] **ClO_3Re**

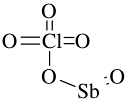


Preparative hazard

See Oxygen: Trirhenium nonachloride

See related METAL HALIDES, METAL OXIDES

4040. Antimony(III) oxide perchlorate
[ ] **ClO_5Sb**

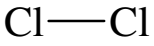


Mellor, 1956, Vol. 2, Suppl. 1, 613

Decomposes with decrepitation above 60°C.

See related METAL PERCHLORATES

4041. Chlorine
[7782-50-5] **Cl_2**



(*MCA SD-80*, 1970); *NSC 207*, 1982; *FPA H39*, 1975; *HCS 1980*, 288 (cyl); *RSC Lab. Hazard Data Sheet No. 30*, 1984

1. Dokter, T., *J. Haz. Mat.*, 1985, **10**, 73—87
2. Anon., *Sichere Chemiearbeit*, 1993, **45**(1), 9
3. Gustin, J.-L., *Chem. Health & Safety*, 2005, **12**(1), 5
4. Anon. *Chem. Eng. News*, 2004 **82**(17) 12

The fire and explosion hazards of chlorine-containing systems have been reviewed [1,3]. A rail tanker of chlorine was being emptied to a chlorine gas distribution network

at 7 bar, when air supply to a pneumatic valve failed, closing the system down. After repair, valve operation caused ignition of the pipework in a chlorine—iron fire, resulting in a leak of chlorine and almost complete destruction of a valve. Ignition is believed to have occurred because the electrolytic chlorine in the system contained 0.7% of hydrogen. Condensation of gaseous chlorine trapped in the pipework (at 0°C) during the shutdown produced a gas phase enriched with hydrogen to within explosive limits and easily ignited, in turn igniting the steelwork [2]. A thorough review of hazards in manufacture and use of chlorine includes assembled flammability data for organic solvents in chlorine atmospheres, and description of improved equipment to extend this study. Nitrogen trichloride is a regular byproduct of chlorine manufacture by brine electrolysis, and has given rise to several accidents after incomplete removal and concentration. Above the tonne scale, liquid chlorine should not be transferred by evaporation, which will concentrate the ppm levels of the residual trichloride permitted [3]. A plant explosion which probably illustrates this is noted [4].
See Hydrogen, below; Steel, below
See CHLORINE-CONTAINING SYSTEMS
See also REPAIR AND MAINTENANCE
See other IGNITION SOURCES

Acetylene MRH 8.70/99+
See Acetylene: Halogens

Air, Ethylene
See Ethylene: Air, Chlorine

Alcohols
See *tert*-Butanol, below
See also HYPOHALITES

Aluminium MRH 5.23/20
Ann. Rep. Chief Insp. Factories, 1953 (Cmd. 9330), 171, HMSO
Corrosive failure of a vaporiser used in manufacture of aluminium chloride caused liquid chlorine to contact molten aluminium. A series of explosions occurred.
See Aluminium: Halogens, or: Oxidants
See Metals, below
See other CORROSION INCIDENTS

Amidosulfuric acid
MCA Guide, 1972, 306
Chlorination of aqueous sulfamic acid led to an explosion from formation of nitrogen trichloride.
See Nitrogen compounds, below (reference 6)

Ammonia
Khattak, M. A., *Engineering Horizons* (Pakistan), 1991, (Aug.), 33
Chlorine reacts with ammonia and compounds to form the treacherously explosive nitrogen trichloride. A change was made to ammonia as refrigerant in the production of liquid chlorine; some months later minor explosions when transferring the chlorine

culminated in several fatalities when the delivery pipe, in which the less volatile trichloride had presumably concentrated by partial evaporation of chlorine, shattered. Further explosions were experienced while decontaminating the plant.
See Nitrogen trichloride
See Preparative hazard, above

Antimony trichloride, Tetramethylsilane
Bush, R. P., Br. Pat. 1 388 991, 1975
Antimony trichloride-catalysed chlorination of the silane to chlorotrimethylsilane in absence of diluent was explosive at 100°C, but controllable at below 30°C.
See other HALOGENATION INCIDENTS

N-Arylsulfinamides
Johnson, C. R. *et al., J. Org. Chem.*, 1983, **48**, 1
Oxidation by chlorine to the arylimidosulfonyl chlorides is sometimes violent, and *tert*-butyl hypochlorite is a milder reagent.

Aziridine MRH 36.98/99+ (?3.6)
See Aziridine: Chlorinating agents

Benzene MRH 2.09/27
1. *491M*, 1975, 102
2. Yakushina, E. P. *et al., Chem. Abs.*, 1981, **94**, 3389

A mixture in the vapour phase exploded when exposed to light [1]. Benzene—chlorine mixtures, though combustible, represent a low explosion hazard [2].
See Hydrocarbons, below

Bis(2,4-dinitrophenyl) disulfide
See Bis(2,4-dinitrophenyl) disulfide: Chlorine

Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.

tert-Butanol
1. Bradshaw, C. P. C. *et al., Proc. Chem. Soc.*, 1963, 213
2. Mintz, M. J. *et al., Org. Synth.*, 1969, **49**, 9

Rate of admission of chlorine into the alcohol during preparation of *tert*-butyl hypochlorite must be regulated to keep the temperature below 20°C to prevent explosion [1]. A safer and simpler preparation uses hypochlorite solution in place of chlorine [2].
See tert-Butyl hypochlorite

Butyl rubber, Naphtha
Komarovskii, N. A. *et al., Chem. Abs.*, 1979, **91**, 158791
Chlorination of butyl rubber in naphtha with chlorine—nitrogen mixtures may lead to explosion if N contents below 77% or Cl contents above 16 % are used.

Caesium oxide
See Caesium oxide: Halogens

Carbon disulfide MRH 1.17/99+

MCA Case History No. 971

When liquid chlorine was added to carbon disulfide in an iron cylinder, an explosion occurred, owing to the iron-catalysed chlorination of carbon disulfide to carbon tetrachloride. The operation had been done previously in glassware without incident.

See other CATALYTIC IMPURITY INCIDENTS

Carbon disulfide, Sodium *aci*-nitromethanide

See Sodium *aci*-nitromethanide: Carbon disulfide, etc.

Chlorinated pyridine, Iron powder

1. Anon., *SciQuest*, 1979, **52**(7), 26—27
2. De Haven, E. S., *Plant/Oper. Progr.*, 1990, **9**(2), 131

An explosion occurred during the preparation of iron(III) chloride from iron powder and chlorine gas in a chlorinated pyridine solvent. This was attributed to formation of iron(II) chloride, its interaction with the solvent to give iron(III) chloride, then reduction of the latter by iron to iron(II) chloride. The exotherm and increasing evolution of hydrogen chloride caused the reactor to fail [1]. Another account of what seems to be the same incident attributes the runaway to Friedel Crafts type polymerisation of trichloromethylpyridines largely present in the reactor [2].

See other GAS EVOLUTION INCIDENTS

2-Chloroalkyl aryl sulfides, Lithium perchlorate

Zefirov, N. S. *et al., Chem. Abs.*, 1986, **104**, 168050

Chlorine scission of 2-chloroheptyl 4-nitrophenyl sulfide or of the 2,4-dinitro analogue in presence of lithium perchlorate formed the explosive 2-chloroheptyl perchlorate in 5—7% yield.

See other ALKYL PERCHLORATES, HALOGENATION INCIDENTS

Chloromethane

Dokter, T., *J. Haz. Mat.*, 1985, **10**, 73—87

The autoignition temperature of chloromethane in presence of chlorine is 215°C, some 400° lower than in presence of air.

3-Chloropropyne

Anon., *Loss Prev. Bull.*, 1974, (001), 10

A vigorous explosion during chlorination of 3-chloropropyne in benzene at 0°C over 4 h was attributed to presence of excess chlorine arising from the slow rate of reaction at low temperature.

See Acetylene: Halogens

See also Hydrocarbons, below (reference 10)

See other HALOGENATION INCIDENTS

Cobalt(II) chloride, Methanol

1. Vlcek, A. A., *Inorg. Chem.*, 1967, **6**, 1425—1427
2. Gillard, R. D. *et al., Chem. & Ind.*, 1973, 77
3. Gillard. R. D., private comm., 1973

During the preparation of *cis*-dichlorobis(2,2’-bipyridyl)cobalt(III) chloride by repeating a published procedure [1], passage of chlorine into an ice-cold solution of

cobalt chloride, bipyridyl and lithium chloride in methanol soon caused an explosion followed by ignition of the methanol inside the reaction vessel. The fire could not be extinguished with carbon dioxide, but went out when the flow of chlorine stopped [2]. This is consistent with the formation and self ignition of methyl hypochlorite in the system at a slightly elevated temperature. An alternative route to the cobalt complex not involving chlorine is available [3].
See Methanol
See also Methanol, below
See also Tetrapyridinecobalt(II)chloride, below
See other HALOGENATION INCIDENTS

Dibutyl phthalate
Statesir, W. A., *Chem. Eng. Progr.*, 1973, **69**(4), 54
A mixture of the ester and liquid chlorine confined in a stainless steel bomb reacted explosively at 118°C.

1,2-Dichloroethane
Steblen, A. V., *Chem. Abs.*, 1981, **95**, 67123
Although some mixtures of the two components will burn, even that with 34% of haloalkane leads only to a 2-fold pressure increase. Such mixtures are comparatively safe.

Dichloro(methyl)arsine
Dillon, K. B. *et al., J. Chem. Soc., Dalton Trans.*, 1976, 1479
In the attempted preparation of tetrachloromethylarsinane ($MeAsCl_4$) by interaction of chlorine with the arsine while slowly warming from —196°C, several sealed ampoules exploded at well below 0°C, probably owing to liberation of chloromethane.
See other GAS EVOLUTION INCIDENTS

Diethyl ether MRH 12.97/21
1. Harrison, G. E., private comm., 1966
2. Unpublished observation, 1949

Chlorine caused ignition of ether on contact [1]. Exposure of an ethereal solution of chlorine to daylight on removal from a fume cupboard caused a mild photocatalysed explosion [2].
See Bromine: Diethyl ether, or: Tetrahydrofuran
See other IRRADIATION DECOMPOSITION INCIDENTS

Diethylzinc MRH 2.22/64
Weast, 1979, C-721
Ignition occurs on contact.

Dimethyl phosphoramidate
1. Block, H. D. *et al., Angew. Chem. (Intern. Ed.)*, 1971, **10**, 491
2. Zwierak, A. *et al., Tetrahedron*, 1970, **26**, 3521
3. Walker, B. J. *et al., Chem. Brit.*, 1979, **15**, 66
4. Walker, B. J. *et al., J. Chem. Soc., Chem. Comm.*, 1980, 462

In a 1.5 g mol preparation of dimethyl *N,N*-dichlorophosphoramidate by chlorination of the ester, a violent explosion occurred during the period of stirring after the reaction. This did not occur on 0.5 g mol scale, and the longer reaction time may have led to liberation of explosive nitrogen trichloride. Suggested precautions include a working scale below 0.2 g mol and short reaction time. The diethyl homologue appears more stable and may be prepared on a kg scale [1]. Another incident involving explosion while following the same preparative procedure [2] was reported some years later [3,4].

Dimethylformamide

Woltornist, A., *Chem. Eng. News*, 1983, **61**(6), 4

After a thermal runaway reaction during chlorination in DMF solution, investigation revealed that saturated solutions of chlorine in DMF are hazardous, and will self-heat and erupt under either adiabatic or non-adiabatic conditions. Principal products are tetramethylformamidinium chloride and carbon dioxide, with dimethylammonium chloride and carbon monoxide in small amounts. A detailed account of the mechanism is to be published.

Dioxan

1. Leclerc-Battin, F. *et al., J. Loss Prevention*, 1991, **4**(3), 170
2. Elaissi, A. *et al., Loss Prevention and Safety Promotion in the Process Industries* Vol II (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 349, Amsterdam, Elsevier, 1995

A study of autoignition of dioxan vapour and chlorine, in the gas phase at rather below 1 atm. Ignition was once observed at 25°C in daylight. In the dark it occurred from 100°C. The maximum pressure rise observed was 26 MPa per sec [1]. Detonation properties of gaseous mixtures of chlorine and dioxane, sometimes diluted with argon, are studied in detail [2]. The combination is more sensitive than most fuel/air mixtures.

Dioxygen difluoride

See Dioxygen difluoride: Various materials

Disilyl oxide

Bailar, 1973, Vol. 1, 1377

Interaction is explosive.

4,4'-Dithiodimorpholine

See 4-Morpholinesulfenyl chloride

Fluorine

See Fluorine: Halogens

Fluoromethylsilane, Dichloromethane

Bürger, H. *et al., Organometallics*, 1993, **12**(12), 4930

Chlorination of the silane in dichloromethane proved uncontrollable even at —100°C. Explosions with decomposition and generation of carbon occurred.

Glycerol

Statesir, W. A., *Chem. Eng. Progr.*, 1973, **69**(4), 54

A mixture of liquid chlorine and glycerol confined in a stainless steel bomb exploded at 70—80°C.

Halocarbons

1. Dokter, T., *J. Haz. Mat.*, 1985, **10**, 75—87
2. *See entry* CHLORINE-CONTAINING SYSTEMS

The auto-ignition temperatures of various halogenated hydrocarbons in presence of chlorine are considerably below the corresponding values in air. Examples are (in °C) chloromethane 215 (618 in air); dichloromethane 262 (556); 1,2-dichloropropane 180 (555°C). Flammability limits are usually wider in chlorine than in air. Gaseous mixtures of chloromethane and chlorine are detonable in the range 12.5—55% [1]. Liquid mixtures of dichloromethane and chlorine may well also be detonable [2].

Hexachlorodisilane

Martin, G., *J. Chem. Soc.*, 1914, **105**, 2859

Hexachlorodisilane vapour ignited in chlorine above 300°C; violent explosions sometimes occurred.

Hydrocarbons, MRH Benzene 2.09/27, acetylene 8.70/99+

1. Mellor, 1956, Vol. 2, Suppl. 1, 380
2. Eisenlohr, D. H., US Pat. 2 989 571, 1961
3. von Schwartz, 1918, 142, 321
4. von Schwartz, 1918, 324
5. Mamadaliev, Y. G. *et al., Chem. Abs.*, 1937, **31**, 8502^5
6. Brooks, B. T., *Ind. Eng. Chem.*, 1924, **17**, 752
7. Johnson, J. H., *Hydrocarbon Proc. Petr. Ref.*, 1963, **42**(2), 174
8. Statesir, W. A., *Chem. Eng. Progr.*, 1973, **69**(4), 52—54
9. de Oliveria, D. B., *Hydrocarbon Proc.*, 1973, **53**(3), 112—126
10. Kilby, J. L., *Chem. Eng. Progr.*, 1968, **64**(6), 52
11. Lawrence, W. W. *et al., Ind. Eng. Chem., Proc. Des. Develop.*, 1970, **9**, 47—49
12. Kokochashvili, V. I. *et al., Chem. Abs.*, 1976, **84**, 20030
13. Rozlovskii, A. I. *et al., Chem. Abs.*, 1976, **84**, 49418
14. Jenkins, P. A., unpublished information, 1974

Interaction of chlorine with methane is explosive at ambient temperature over yellow mercury oxide [1], and mixtures containing above 20 vol % of chlorine are explosive [2]. Mixtures of acetylene and chlorine may explode on initiation by sunlight, other UV source, or high temperatures, sometimes very violently [3]. Mixtures with ethylene explode on initiation by sunlight, etc., or over mercury, mercury oxide or silver oxide at ambient temperature, or over lead oxide at 100°C [1,4]. Interaction with ethane over activated carbon at 350°C has caused explosions, but added carbon dioxide reduces the risk [5]. Accidental introduction of gasoline into a cylinder of liquid chlorine caused a slow exothermic reaction which accelerated to detonation. This effect was verified [6]. Injection of liquid chlorine into a naphtha—sodium hydroxide mixture (to generate hypochlorite in situ) caused a violent explosion. Several other incidents involving violent reactions of saturated hydrocarbons with chlorine were noted [7].

In a review of incidents involving explosive reactivity of liquid chlorine with various organic auxiliary materials, two involved hydrocarbons. A polypropylene filter element fabricated with zinc oxide filler reacted explosively, rupturing the steel case previously tested to over 300 bar. Zinc chloride derived from the oxide may have initiated the runaway reaction. Hydrocarbon-based diaphragm pump oils or metal-drawing waxes were violently or explosively reactive [8]. A violent explosion in a wax chlorination plant may have involved unplanned contact of liquid chlorine with wax or chlorinated wax residues in a steel trap. Corrosion products in the trap may have catalysed the runaway reaction, but hydrogen (also liberated by corrosion in the trap) may also have been involved [9].

During maintenance work, simultaneous release of chlorine and acetylene from two plants into a common vent line leading to a flare caused an explosion in the line [10]. The violent interaction of liquid chlorine injected into ethane at 80°C/10 bar becomes very violent if ethylene is also present [11]. The relationship between critical pressure and composition for self-ignition of chlorine—propane mixtures at 300°C was studied, and the tendency is minimal for 60:40 mixtures. Combustion is explosive under some conditions [12]. Precautions to prevent explosions during chlorination of solid paraffin hydrocarbons are detailed [13]. In the continuous chlorination of polyisobutene at below 100°C in absence of air, changes in conditions (increase in chlorine flow, decrease in polymer feed) leading to over-chlorination caused an exotherm to 130°C and ignition [14].

See Benzene, above; Methane, Oxygen, etc., or Synthetic rubber, both below

See also TURPENTINE: Halogens

Hydrocarbons, Lewis acids

Howard, W. B., *Loss Prev.*, 1973, **7**, 78

During chlorination of hydrocarbons with Lewis acid catalysis, the catalyst must be premixed with the hydrocarbon before admission of chlorine. Addition of catalyst to the chlorine—hydrocarbon mixture is very hazardous, causing instantaneous release of large volumes of hydrogen chloride.

See Iron(III) chloride, Monomers, below

See other GAS EVOLUTION INCIDENTS, HALOGENATION INCIDENTS

Hydrochloric acid, Dinitroanilines

See Hydrogen chloride: Chlorine, Dinitroanilines

Hydrogen MRH 2.55/3

1. Mellor, 1956, Vol. 2, Suppl. 1, 373—375
2. Weissweiler, A., *Z. Elektrochem.*, 1936, **42**, 499
3. Eichelberger, W. C. *et al., Chem. Eng. Progr.*, 1961, **57**(8), 94
4. Wood. J. L., *Loss Prev.*, 1969, **3**, 45—47
5. Stephens, T. J. R. *et al., Paper 62B*, 65th AIChE Meeting, New York, 1972
6. de Oliveria, D. B., *Hydrocarbon Proc.*, 1973,**52**(3), 112—126
7. Antonov, V. N. *et al., Chem. Abs.*, 1974, **81**, 172184
8. Frolov, U. E., *Chem. Abs.*, 1977, **87**, 119999
9. Anon., *Fire Prev.*, 1986, (189), 43

Combination of the elements may be explosive over a wide range of physical conditions, with initiation by sparks, radiant energy or catalysis, e.g. by yellow mercuric oxide at ambient temperature [1]. There is a narrow range of concentrations in which the mixture is supersensitive to initiation [2]. Explosion—detonation phenomena in chlorine production cells have been investigated [3,4]. The explosive limits of the mixture vary with the container shape and method of initiation, but are usually within the range 5—89% of hydrogen by volume [1]. After an explosion in a chlorine distillate receiver where hydrogen had been produced by corrosion, no initiation source could be identified or reasonably postulated following a thorough investigation [5]. Several other hydrogen—chlorine explosions without identifiable ignition sources are also mentioned. Hydrogen may have been involved in a severe wax chlorinator explosion [6]. Pressure increase during explosive combustion of mixtures within the critical concentration region of 5—15 vol % of hydrogen was studied, and found less than anticipated [7]. Critical self-ignition temperatures are 397—284°C for mixtures containing 8—18% of hydrogen [8]. A faulty non-return valve allowed hydrogen to leak into a fibreglass-reinforced pipeline containing chlorine, and spontaneous ignition and explosion occurred [9].

Hydrogen, Nitrogen trichloride

See Nitrogen trichloride: Chlorine, Hydrogen

Hydrogen, Other gases

Munke, K., *Chem. Technik*, 1974, **26**, 292—295

Available data on explosibility of chlorine and hydrogen in admixture with air, hydrogen chloride, oxygen or inert gases is discussed and presented as triangular or rectangular diagrams.

See Sodium chlorate: Preparative hazard

Hydrogen(?), Sulfuric acid

Tabata, Y. *et al., Chem. Abs.*, 1984, **100**, 90601

Chlorine gas, produced by electrolysis of brine, was dried by passage through a mist of sulfuric acid in a drying tower, where static charge was generated. An explosion in the tower, (presumably involving hydrogen as fuel) was attributed to initiation by static spark.

See Hydrogen: Oxygen, Sulphuric acid

See other STATIC INITIATION INCIDENTS

Iron(III) chloride, Monomers

1. *MCA Case History No. 2115*
2. *MCA Case History No. 2147*

During chlorination of styrene in carbon tetrachloride at 50°C, a violent reaction occurred when some 10% of the chlorine gas had been fed in. Laboratory examination showed that the eruption was caused by a rapid polymerisation reaction catalysed by ferric chloride [1]. Various aromatic monomers decomposed in this way when treated with gaseous chlorine or hydrogen chloride (either neat, or in a solvent) in the presence of steel or iron(III) chloride. Exotherms of 90°C (in 50% solvent) to 200°C (no solvent) were observed, and much gas and polymeric residue was forcibly ejected.

See Hydrocarbons, Lewis acids, above

Mercury(II) oxide
See Mercury(II) oxide: Chlorine

Metal acetylides and carbides
The mono- and di-alkali metal acetylides, copper acetylides, iron, uranium and zirconium carbides all ignite in chlorine, the former often at ambient temperature.
See Caesium acetylide: Halogens
Dicopper(I) acetylide: Halogens
Iron carbide: Halogens
Lithium acetylide: Halogens
Monocaesium acetylide
Monorubidium acetylide
Strontium acetylide: Halogens
Uranium dicarbide: Halogens
Zirconium dicarbide: Halogens
See Monolithium acetylide—ammonia: Gases

Metal hydrides MRH Calcium hydride 5.35/37, Potassium hydride 4.98/52
Mellor, 1941, Vol. 2, 483; Vol. 3, 73
Potassium, sodium and copper hydrides all ignite in chlorine at ambient temperatures.

Metal phosphides MRH Magnesium phosphide 4.04/39
See Copper(II) phosphide: Oxidants

Metals MRH values below references

1. Mellor, 1941, Vol. 2, 92, 95; 1956, Vol. 2, Suppl. 1, 380, 469; 1941, Vol. 3, 638; 1940, Vol. 4, 267, 480; 1941, Vol. 7, 208, 260, 436; 1941, Vol. 9, 379, 626, 849; 1942, Vol. 12, 312; Vol. 15, 146
2. Hanson, B. H., *Process Eng.*, 1975, (2), 77
3. Davies, D. J., *Process Eng.*, 1975, (2), 77
4. Anon., *Loss Prev. Bull.*, 1975, (006), 1
5. Anon., *Loss Prev. Bull.*, 1991, (097), 9

MRH Aluminium 5.23/20, bismuth 1.21/66, calcium 7.15/36, copper 1.55/47, germanium 2.51/34, magnesium 6.78/25, manganese 3.85/44, nickel 2.34/45, potassium 5.81/53, sodium 6.98/40, tin 2.47/45, vanadium 3.72/42, zinc 3.05/48

Tin ignites in liquid chlorine at —34°C, aluminium powder in the gas at —20°C, while vanadium powder explodes on contact at 0°C with the pressurised liquid. A solution in heptane ignites with powdered copper well below 0°C. Aluminium, brass foil, calcium powder, copper foil, iron wire, manganese powder, and potassium all ignite in the dry gas at ambient temperature, as do powdered antimony, bismuth and germanium sprinkled into the gas, while magnesium, sodium and zinc ignite in the moist gas. Thorium, tin and uranium ignite and incandesce on warming (uranium to 150°C), powdered nickel burns at 600°C, while mercury at 200—300°C ignites in a stream of chlorine. Aluminium—titanium alloys also ignite on heating in chlorine, and niobium ignites on gentle warming [1]. Unlike most other metals, titanium is not suitable for components in contact with *dry* gaseous or liquid chlorine, as ignition may occur [2]. Minimum water content to prevent attack may be from 0.015 to 1.5%, depending on conditions [3]. A statement on ignition of titanium in wet chlorine is

incorrect [4]. Titanium washers were fitted to a liquid chlorine line due to mislabelling. Within an hour of exposure to chlorine they burnt through in a 'puff of smoke' followed by a chlorine leak [5].
See Aluminium, above; Steel, below
See also Beryllium: Halogens

Methane, Oxygen
Mal'tseva, A. S. *et al., Chem. Abs.*, 1982, **96**, 90922
Ignition in an oxychlorination reactor was attributed to the presence of free space above the packed reaction zone. Other hazards are discussed.

Methanethiol
Tullo, A., *Chem. Eng. News*, 2001, **79**(30), 11
A partial account of an explosion, fire and methanethiol release at a site where chlorine and methanethiol tankers were adjacent to each other for unloading. One may surmise that wrong connection allowed contact in the pipework, the two react readily.

Methanol
Trans. US Natl. Safety Congr., 1937, 273
Passage of chlorine through cold recovered methanol (but not fresh methanol) led to a mild explosion and ignition, formation of methyl hypochlorite apparently being catalysed by an impurity.
See Bromine: Alcohols
See Cobalt(II) chloride, Methanol, above; Methanol, Tetrapyridinecobalt(II) chloride, below
See other CATALYTIC IMPURITY INCIDENTS

Methanol, Tetrapyridinecobalt(II) chloride
Glerup, J. *et al., Acta Chem. Scand., Ser. A*, 1978,**A32**, 673
In preparation of dichlorotetrapyridinecobalt(III) chloride by oxidation of the Co(II) salt in methanol solution with gaseous chlorine, severe explosions (formation of methyl hypochlorite) have occurred. Use of liquid chlorine at —40°C to effect oxidation is uneventful.
See Cobalt(II) chloride, Methanol, above

Nitrogen compounds MRH values below references

1. Mellor, 1941, Vol. 2, 95; 1940, Vol. 8, 99, 288, 313, 607
2. Bowman, W. R. *et al., Chem. & Ind.*, 1963, 979
3. Bainbridge, E. G., *Chem. & Ind.*, 1963, 1350
4. Folkers, K. H. *et al., J. Amer. Chem. Soc.*, 1941,**63**, 3530
5. King, J. F. *et al., Synthesis*, 1980, 285
6. Schierwater, F.-W., *Major Loss Prevention*, 1971, 49
7. Sorbe, 1968, 120
8. Kirk-Othmer, 1964, Vol. 5, 2
9. Dokter, T., *J. Haz. Mat.*, 1985, **10**, 207—224
10. Nothe, M. *eyt al., Inorg. Chem.*, 1996, **35**(15), 4529

MRH Ammonia 1.88/14, hydrazine 2.43/19, hydroxylamine 3.22/49, calcium nitride 5.90/41

Ammonia—chlorine mixtures are explosive if warmed or if chlorine is in excess, owing to formation of nitrogen trichloride. Hydrazine, hydroxylamine and calcium nitride ignite in chlorine, and nitrogen triiodide may explode on contact with chlorine [1]. During chlorination of impure biuret in water at 20°C, a violent explosion occurred [2]. This was attributed to conversion of the cyanuric acid impurity (3%) to nitrogen trichloride and spontaneous explosion of the latter [3]. During interaction of chlorine and alkylthiouronium salts to give alkanesulfonyl chlorides, the dangerously explosive nitrogen trichloride may be produced if excess chlorine or slow chlorination is used. General precautions are discussed [4]. More recently it has been recommended that prompt working up of the reaction mixture will avoid formation of nitrogen trichloride [5]. Aziridine readily gives the explosive *N*-chloro compound. During chlorination of 2,4,6-triketo-hexahydro-1,3,5-triazine (cyanuric acid), presence of the diaminoketo and aminodiketo analogues as impurities, or of an unusually low pH value, may lead to formation of nitrogen trichloride. UV irradiation may be used to destroy this in a continuous circulation reactor and prevent build-up of dangerous concentrations [6]. Chlorination of amidosulfuric acid [7] or acidic ammonium chloride solutions [8] gives the powerfully explosive oil, nitrogen trichloride. The formation and separation of nitrogen trichloride have been studied in detail [9,10].

See N-HALOGEN COMPOUNDS

Non-metal hydrides MRH Diborane 3.59/12, phosphine 2.13/11

Mellor, 1939, Vol. 9, 55, 396; 1939, Vol. 8, 65; 1940, Vol. 6, 219; 1941, Vol. 5, 37

Arsine, phosphine and silane all ignite in contact with chlorine at ambient temperature, while diborane and stibine react explosively, the latter also with chlorine water.

See Ethylphosphine: Halogens

Non-metals

Mellor, 1941, Vol. 2, 292; 1956, Vol. 2, Suppl. 1, 380; 1943, Vol. 11, 26

Liquid chlorine at —34°C explodes with white phosphorus, and a solution in heptane at 0°C ignites red phosphorus. Boron, active carbon, silicon and phosphorus all ignite in contact with gaseous chlorine at ambient temperature. Arsenic incandesces on contact with liquid chlorine at —34°C, and the powder ignites when sprinkled into the gas at ambient temperature. Tellurium must be warmed slightly before incandescence occurs.

Other reactants

1. 1. Yoshida, 1980, 61—62
2. 2. Gustin, J. J. *et al., Loss Prevention and Safety Promotion in the Process Industries*, Vol I, (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 157, Amsterdam, Elsevier, 1995

MRH values calculated for 31 combinations with oxidisable materials are given [1]. Flammability limits and auto-ignition temperatures for a number of mixtures with organic fuels are measured and reviewed. All experimental work reported is in the vapour phase, detonation is common. Precautions for chlorination reactions are considered [2].

Oxygen difluoride

See Oxygen difluoride: Halogens

Phenylmagnesium bromide

1. Datta, R. L. *et al., J. Amer. Chem. Soc.*, 1919, **41**, 287
2. Zakharkin, L. I. *et al., J. Organomet. Chem.*, 1970, **21**, 271

After treatment of the Grignard reagent with chlorine, the solid which separated exploded when shaken [1]. This solid was not seen later, using either diethyl ether or THF as solvent [2]. (The explosive solid could have been magnesium hypochlorite if moisture were present in the chlorine.)

See Magnesium hypochlorite

Phosphorus compounds MRH values below references

1. Mellor, 1940, Vol. 8, 812, 842, 844—845, 897
2. von Schwartz, 1918, 324

MRH Phosphine 2.13/11, phosphorus trioxide 0.46/43, magnesium phosphide 4.02/39

Borondiiodophosphide, phosphine, phosphorus trioxide and trimercury tetraphosphide all ignite in contact with chlorine at ambient temperature. Trimagnesium diphosphide and trimanganese diphosphide ignite in warm chlorine [1], while ethylphosphine explodes with chlorine [2]. Unheated boron phosphide incandesces in chlorine.

See Trimethyl thionophosphate, below

Polychlorobiphenyl

Statesir, W. A., *Chem. Eng. Progr.*, 1973, **69**(4), 53—54

A mixture of a polychlorobiphenyl process oil and liquid chlorine confined in a stainless steel bomb reacted exothermally between 25 and 81°C.

Preparative hazard (electrolysis)

1. Anon., *Fire Prevention*, 1986, (189), 43.
2. Kucinski R.E. *et al., Mod. Chlor-Alkali Technol.*, 1995, 6, 89
3. Gustin, J.-L., *Chem. Health & Safety*, 2005, **12**(1), 5

A fire and explosions caused by hydrogen from a chloralkali plant seeping through a defective non-return valve, then spontaneously igniting is reported [1]. A consideration of the risks of producing hydrogen chlorine mixtures, related to the design of plant in question, claims the ion-exchange membrane plant to be safest [2]. Electrolysis of brines regularly produces low levels of nitrogen trichloride from nitrogenous impurities as byproduct, this concentrates when liquid chlorine is evaporated and should be largely removed by distillation before the product is sold [3].

See Ammonia, below

See Sodium chloride: Nitrogen compounds

Silicones

Statesir, W. A., *Chem. Eng. Progr.*, 1973, **69**(4), 53—54

Silicone process oils mixed with liquid chlorine confined in a stainless steel bomb reacted explosively on heating; polydimethysiloxane at 88—118°C, and polymethyltrifluoropropylsiloxane at 68—114°C. Previously, leakage of a silicone pump oil into a liquid chlorine feed system had caused rupture of a stainless steel ball valve under a pressure surge of about 2 kbar.

Sodium hydroxide

MCA Case History No. 1880

Attempted disposal of a small amount of liquid chlorine by pouring it into 20% sodium hydroxide solution caused a violent reaction leading to personal contamination.

Steel

1. *MCA Case History No. 608*
2. Stephens, T. J. R. *et al., Paper 62B*, 65th AIChE Meeting, New York, 1972
3. Vervalin, 1973, 85
4. Schwarz, E., *Proc. 3rd Int. Symp. Prev. Occ. Risks Chem. Ind.*, 429—434, Heidelberg, ISSA, 1976
5. Fishwick, T., *Loss Prev. Bull.*, 1998, 139, 12
6. Anon., *Loss. Prev. Bull.*, 1983, (052), 7

Chlorine leaking into a steam-heated mild steel pipe caused ignition of the latter at about 250°C [1]. Sheet steel in contact with chlorine usually ignites at 200—250°C, but the presence of soot, rust, carbon or other catalysts may reduce the ignition temperature to 100°C. Dry steel wool ignites in chlorine at only 50°C [2]. Use of a carbon steel inlet pipe in a paraffin chlorination system led to rupture of the pipe and a fire [3]. Presence of an organic contaminant in a steel liquid chlorine vaporiser operating at 50°C led to local exothermic heating to 140—150°C and an iron—chlorine fire ensued. In another incident, admission of chlorine gas into a recently-welded (warm) steel pipe again led to a fire [4]. Another account of the same, or a very similar, vaporiser fire is found in [5]. When steel tanks containing chlorine are exposed to fire conditions, the tank wall above the liquid level may soon attain a temperature at which combustion of steel in chlorine will occur, perforating the tank. Two incidents involving derailed chlorine tank cars are described [6].

See other CORROSION INCIDENTS, IGNITION SOURCES

Sulfides

Mellor, 1940, Vol. 4, 952; 1946, Vol. 6, 144; 1939, Vol. 9, 270

Arsenic disulfide, boron trisulfide and mercuric sulfide all ignite in chlorine at ambient temperature, the first only in a rapid stream.

Synthetic rubber

Murray, R. L., *Chem. Eng. News*, 1948, **26**, 3369

During interaction of synthetic rubber and liquid chlorine, a violent explosion occurred. It is known that natural and synthetic rubbers will burn in liquid chlorine.

See Hydrocarbons, above

Tetraselenium tetranitride

See Tetraselenium tetranitride

Trialkyl boranes

Coates, 1967, Vol. 1, 199

The lower homologues tend to ignite in chlorine or bromine.

Trimethyl thionophosphate

MCA Case History No. 371

At an early stage in the preparation of methyl parathion, it is supposed that the phosphorus ester was being chlorinated to give dimethyl thionophosphorochloridate. Thermocouple failure indicated a low reaction temperature and the process controller boosted the chlorine feed rate, but when this fault situation was realised, the chlorine flow and agitator were stopped. However, an exothermic runaway reaction developed, eventually leading to a violent explosion.

See other RUNAWAY REACTIONS

Tungsten dioxide

Mellor, 1943, Vol. 11, 851

Incandescence on warming.

Water

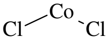
1. Kosharov, P., *Chem. Abs.*, 1940, **34**, 3917q
2. Bray, A. W., private comm., 1982

The statement that 'Mixtures of chlorine and water at certain concentrations are capable of explosion by spark ignition' [1] should read 'Mixtures of chlorine and hydrogen...' [2].

See other HALOGENS, OXIDANTS

4042. Cobalt(II) chloride

[7646-79-9] **Cl_2Co**



HCS 1980, 320

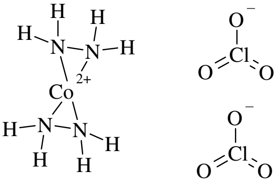
Metals

See Potassium: Metal halides
Sodium: Metal halides

See other METAL HALIDES

4043. Dihydrazinecobalt(II) chlorate

[ ] **$Cl_2CoH_8N_4O_6$**



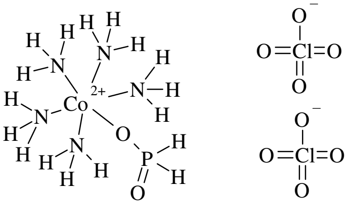
Salvadori, R., *Gazz. Chim. Ital. [2]*, 1910, **40**, 9

It explodes powerfully on the slightest impact or friction, or on heating to 90°C.

See other AMMINEMETAL OXOSALTS

4044. Pentaamminephosphinatocobalt(III) perchlorate

[ ] **$Cl_2CoH_{17}N_5O_{10}P$**



Anon., *BCISC Quart. Safety Summ.*, 1965, **36**, 58

When a platinum wire (which may have been hot) was dipped for a flame test into a sintered funnel containing the air-dried complex, detonation occurred. This may have been due to heat and/or friction on a compound containing both strongly oxidising and reducing radicals. Avoid dipping (catalytically active) platinum wire into bulk samples of materials of unknown potential.

See other AMMINEMETAL OXOSALTS, REDOX COMPOUNDS

4045. Cobalt(II) perchlorate hydrates

[13478-33-6, 33827-55-3, 73954-59-3] (6, 4, $2H_2O$, resp.) **$Cl_2CoO_8.xH_2O$**

$Co(ClO_4)_2.xH_2O$

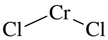
1. Salvadori, R., *Gazz. Chim. Ital. [2]*, 1910, **40**, 15—16
2. Robinson, P. J., private comm., 1982
3. Robinson, P. J., *Nature*, 1981, **293**, 696
4. Cook, R. E. *et al., J. Chem. Res. (S)*, 1982, 267 (*M*, 2772—2783)
5. Cook, R. E. *et al., Chem. Brit.*, 1982, **18**, 859

In view of the ready commercial availability and apparent stability of the hexahydrate, it is probable that the earlier report of explosion on impact, and deflagration on rapid heating [1] referred to the material produced by partial dehydration at 100°C, rather than the hexahydrate [2]. The caked crystalline hydrated salt, prepared from aqueous perchloric acid and excess cobalt carbonate with subsequent heated evaporation, exploded violently when placed in a mortar and tapped gently to break up the crystalline mass, when a nearby dish of the salt also exploded [3]. Subsequent investigation revealed the probable cause as heating the solid stable hexahydrate to a temperature (~150°C) at which partial loss of water produced a lower and endothermic hydrate (possibly a trihydrate) capable of explosive decomposition. This hazard may also exist for other hydrated metal perchlorates, and general caution is urged [4,5].

See other METAL PERCHLORATES, SOLVATED OXOSALT INCIDENTS

4046. Chromium(II) chloride

[10049-05-5] **Cl_2Cr**



Water

1. *MCA Case History No. 1660*
2. Bretherick, L., *Chem. Brit.*, 1976, **12**, 204

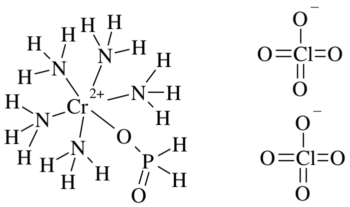
An unopened bottle of chromous chloride solution exploded after prolonged storage [1]. This was most likely caused by internal pressure of hydrogen developed by slow reduction of the solvent water by the powerfully reducing Cr(II) ion [2].

See Chromium(II) sulfate

See other GAS EVOLUTION INCIDENTS, METAL HALIDES, REDUCANTS

4047. Pentaamminephosphinatochromium(III) perchlorate

[65901-39-5] **$Cl_2CrH_{17}N_5O_{10}P$**



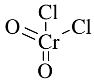
Coronas, J. M. *et al., Inorg. Chim. Acta*, 1977, **25**, 110

A sample detonated violently on heating.

See other AMMINEMETAL OXOSALTS, REDOX COMPOUNDS

4048. Chromyl chloride

[14977-61-8] **Cl_2CrO_2**



1. Sidgwick, 1950, 1004
2. Pitwell, L. R., private comm., 1964

Though a powerful and often violent oxidant of inorganic and organic materials in absence of a diluent, it has found use as solutions in preparative organic chemistry for the controlled oxidation of alkyl aromatic derivatives [1]. In such a reaction, failure of a stirrer during addition of the chloride caused a build-up of unreacted material, followed by a violent explosion [2].

See other AGITATION INCIDENTS

Ammonia

Mellor, 1943, Vol. 11, 394

Contact with ammonia causes incandescence.

Isopropylcyclopropane

Wang, K. *et al., J. Org. Chem.*, 1997, **62**(13), 4248

A violent reaction was experienced on adding this hydrocarbon to the chloride at room temperature. They can be safely mixed at —78°C.

Non-metal halides

1. Mellor, 1943, Vol. 11, 394—395
2. Pascal, 1959, Vol. 14, 153

A jet of chromyl chloride vapour ignites in the vapour of disulfur dichloride, and addition of drops of chromyl chloride to cooled phosphorus trichloride causes incandescence and sometimes explosion [1]. Phosphorus tribromide may also ignite with the chloride [2].

Non-metal hydrides

Pascal, 1959, Vol. 14, 153

Hydrogen sulfide or phosphine may ignite in contact with the chloride.

Non-metals

Mellor, 1943, Vol. 11, 394—395

Moist phosphorus explodes in contact with chromyl chloride, while flowers of sulfur ignites.

Organic solvents

Mellor, 1943, Vol. 11, 396

Acetone, ethanol or ether ignite on contact with the chloride, and turpentine behaves similarly.

Sodium azide

Mellor, 1967, Vol. 8, Suppl. 2.2, 36

Interaction of chromyl chloride and sodium azide to form chromyl azide is explosive in absence of a diluent.

Urea

Pascal, 1959, Vol. 14, 153

Urea ignites in contact with chromyl chloride.

Water

Partington, 1966, 751

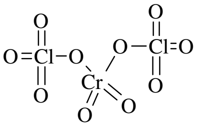
Hydrolysis of chromyl chloride is violent.

See other OXIDANTS

See related METAL HALIDES

4049. Chromyl perchlorate

[62597-99-3] **Cl_2CrO_{10}**



Alone, or Organic solvents

Schmeisser, M., *Angew. Chem.*, 1955, **67**, 499

A powerful oxidant which may explode violently above 80°C, and which causes organic solvents to ignite on contact. It decomposes on exposure to light, usually slowly, sometimes explosively.
See other OXIDANTS
See related METAL PERCHLORATES

4050. Copper(I) chloride

[7758-89-6] **Cl_2Cu_2**

$Cl^- \; Cu^+{-}Cu^+ \; Cl^-$

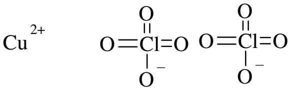
HCS 1980, 337

Lithium nitride
See Lithium nitride: Copper(I) chloride
See other METAL HALIDES

Preparative hazard
See Copper: Complexing agents, Water

4051. Copper(II) perchlorate

[10294-46-9] **Cl_2CuO_8**



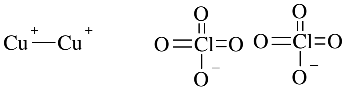
$Cu^{2+} \quad O{=}\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{Cl}}{=}O \quad O{=}\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{Cl}}{=}O$

Polyfunctional amines
Fabbrizzi, L. *et al., J. Chem. Soc., Dalton Trans.*, 1984, 1496
Complexes formed with the extended chain polyfunctional amines $H_2N[CH_2]_nNH[CH_2]_mNH[CH_2]_nNH_2$($n$ or m = 2 or 3) may be explosive and must be handled with care.
See related AMMINEMETAL OXOSALTS, [14] DIENE-N_4 COMPLEXES

N-(2-Pyridyl)acylacetamides
Illiopoulos, P. *et al., J. Chem. Soc., Dalton Trans.*, 1986, 437—443
The dihydrated binuclear complexes between copper(II) perchlorate and *N*-(2-pyridyl)-acetoacetamide and -benzoylacetamide, $[Cu_2L_2(ClO_4)_2] \cdot 2H_2O$, exploded on heating to 260°C.
See other METAL PERCHLORATES
See related AMMINEMETAL OXOSALTS, [14] DIENE-N_4 COMPLEXES

4052. Copper(I) perchlorate

[15061-57-1] **$Cl_2Cu_2O_8$**



Alkenes, or Carbon monoxide

1. Ogura, T., *Inorg. Chem.*, 1976, **15**, 2301—2303
2. Thompson, J. S. *et al., Inorg. Chem.*, 1984, **23**, 2814

If preparation of the perchlorate (by stirring copper(II) perchlorate in water with copper powder) is effected under an atmosphere of the ligands ethylene, allene, 1,3-butadiene or carbon monoxide, two types of explosive complexes, $L_2 . Cu_2(ClO_4)_2 . nH_2O$, (L represents one double bond), are formed. There is a crystalline series with n = 4, e.g. $2CO . Cu_2(ClO_4)_2 . 4H_2O$, and an amorphous series with n = 3, e.g. $C_3H_4 . Cu_2(ClO_4)_2 . 3H_2O$. All the complexes are explosive, but unpredictably so. Sometimes a complex would not explode under a hammer-blow, but sometimes it would explode on stirring with a Teflon-coated stirrer bar. On one occasion a 10 mg sample stored in glass exploded, propelling glass fragments 10 m [1]. When the ethylene complex is prepared in methanol solution, it must not be allowed to dry out or it will explode [2].

1,4-Oxathiane

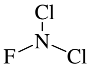
Barnes, J. C. *et al., J. Chem. Soc. Pak.*, 1982, **4**, 103—113

Of the two complexes which the perchlorate forms with oxathiane (1:3, 1:4), the latter explodes on heating.

See other METAL PERCHLORATES, REDOX COMPOUNDS

4053. Dichlorofluoramine

[17417-38-8] **Cl_2FN**



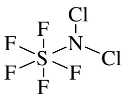
1. Sukornick, B. *et al., Inorg. Chem.*, 1963, **2**, 875
2. Batty, W. E., *Chem. & Ind.*, 1969, 1232

In the liquid phase, it is an extremely friction- and shock-sensitive explosive [1], like the trichloro analogue [2].

See other N-HALOGEN COMPOUNDS

4054. *N,N*-Dichloropentafluorosulfanylamine

[22650-46-0] **Cl_2F_5NS**



Kirk Othmer, 4th Edn., 1993, Vol IV, 917
Shock sensitive and unstable from 80°C.

Preparative hazard

Waterfeld, A. *et al., J. Chem. Soc., Chem. Comm.*, 1982, 839

Reaction of chlorine fluoride with trifluorosulfur nitride is rather hazardous and may lead to violent explosions. A safer alternative preparation is to use chlorine and mercuric fluoride in place of chlorine fluoride.

See other N-HALOGEN COMPOUNDS, N—S COMPOUNDS

4055. Iron(II) chloride

[7758-94-3] **Cl_2Fe**

Cl—Fe—Cl

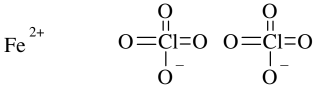
Ozonides

See OZONIDES: METALS

See other METAL HALIDES, REDUCANTS

4056. Iron(II) perchlorate

[13933-23-8] **Cl_2FeO_8**



$Fe^{2+}\ (O_3ClO^-)_2$

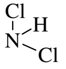
Preparative hazard

See Perchloric acid: Iron(II) sulfate

See other METAL PERCHLORATES, REDOX COMPOUNDS

4057. Dichloramine (Chlorimide)

[3400-09-7] **Cl_2HN**



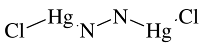
Eckert, P. *et al., Chem. Abs.*, 1951, **45**, 7527g

Dissolving *N,N,N*',N'-tetrachloroadipamide in boiling water gives a highly explosive oil, probably dichloramine.

See other N-HALOGEN COMPOUNDS

4058. *N,N′*-Bis(chloromercurio)hydrazine

[ ] **$Cl_2H_2Hg_2N_2$**



Mellor, 1940, Vol. 4, 874, 881; Vol. 8, 318

It explodes when heated or struck, and the bromo and other analogues are similar.

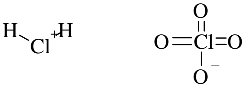
See Mercury(II) chloride: Hydrazine salts, Base

See other MERCURY COMPOUNDS

See related METAL HYDRAZIDES

4059. Chloronium perchlorate

[ ] **$Cl_2H_2O_4$**



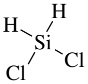
Hantzsch, A., *Ber.*, 1930, **63**, 1789

This hydrogen chloride—perchloric acid complex spontaneously dissociates with explosive violence.

See other NON-METAL PERCHLORATES

†4060. Dichlorosilane

[4109-96-0] **Cl_2H_2Si**



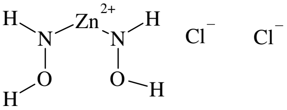
1. Sharp, K. G. *et al., J. Electrochem. Soc.*, 1982, **129**
2. Britton, L. G., *Plant/Oper. Progr.*, 1990, **9**(1), 16

It is unusual in being flammable with so high a chlorine content (70%), and mixtures with air may detonate if confined when ignited. One case of spontaneous ignition under ambient conditions was observed [1]. It has an unusually low autoignition temperature (43±3°C). A survey of hazards and combustion is found in [2]. There is a risk of combustion with fluorochloromethanes. Autoignition was observed on contact with traces of a mixture of alkali nitrates/ nitrite.

See other HALOSILANES

4061. Bis(hydroxylamine)zinc chloride

[33774-96-8] **$Cl_2H_6N_2O_2Zn$**



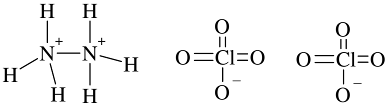
Walker, J. E. *et al., Inorg. Synth.*, 1967, **9**, 2

It explodes at 170°C.

See related AMMINEMETAL HALIDES

4062. Hydrazinium diperchlorate

[13812-39-0] **$Cl_2H_6N_2O_8$**



Grelecki, C. J. *et al., ACS 54*, 1966, 73

The thermal decomposition of this solid rocket propellant component has been studied.

Metal compounds

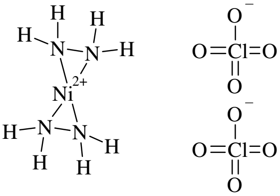
Probhakaran, C. *et al., Def. Sci. J.*, 1982, **31**, 285—291

Of the series of additives copper chromate, copper chloride, nickel oxide, iron(III) oxide or magnesium oxide, the earlier members have the greatest effect in increasing the sensitivity of the explosive salt towards heat, impact or friction.

See other PERCHLORATE SALTS OF NITROGENOUS BASES

4063. Bis(hydrazine)nickel perchlorate

[ ] **$Cl_2H_8N_4NiO_8$**



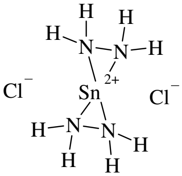
Maissen, B. *et al., Helv. Chim. Acta*, 1951, **34**, 2084—2085

The salt, known to be explosive when heated dry (but not under a hammer-blow), exploded violently when stirred as a dilute aqueous suspension.

See other AMMINEMETAL OXOSALTS

4064. Bis(hydrazine)tin(II) chloride

[55374-98-6] **$Cl_2H_8N_4Sn$**



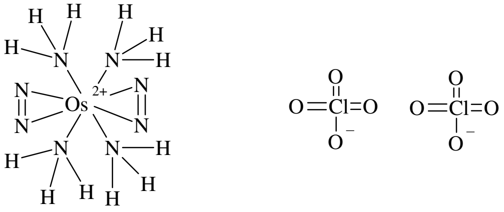
Mellor, 1941, Vol. 7, 430

It explodes on heating.

See related AMMINEMETAL HALIDES, METAL HYDRAZIDES

4065. Tetraamminebis(dinitrogen)osmium(II) perchlorate

[ ] **$Cl_2H_{12}N_8O_8Os$**



Creutz, C. A., private comm., 1969

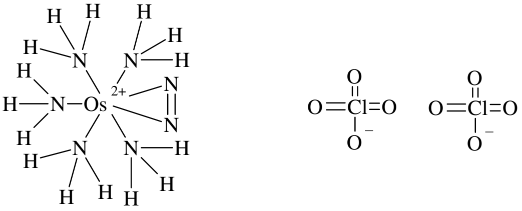
The dry salt may explode on touching.

See next entry below

See other AMMINEMETAL OXOSALTS

4066. Pentaamminedinitrogenosmium(II) perchlorate

[20611-53-4] **$Cl_2H_{15}N_7O_8Os$**



Bohr, J. D. *et al., Inorg. Chem.*, 1980, **19**, 2417

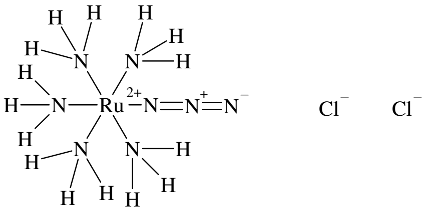
It can be detonated.

See entry next above

See other AMMINEMETAL OXOSALTS

4067. Pentaammineazidoruthenium(III) chloride

[28223-30-5] (ion) **$Cl_2H_{15}N_8Ru$**



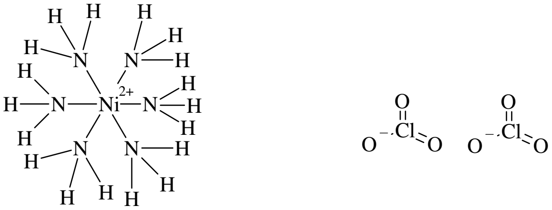
Hazardous intermediate

See Pentaamminechlororuthenium chloride: Sodium azide

See related METAL AZIDES

4068. Hexaamminenickel chlorate

[ ] **$Cl_2H_{18}N_6NiO_6$**



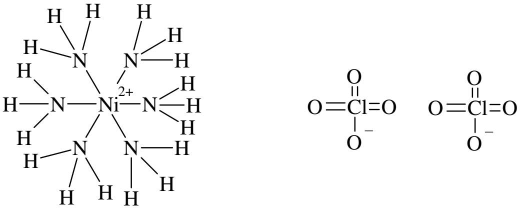
Mellor, 1956, Vol. 2, Suppl. 1, 592

It explodes on impact.

See other AMMINEMETAL OXOSALTS

4069. Hexaamminenickel perchlorate

[14322-50-0] **$Cl_2H_{18}N_6NiO_8$**



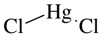
Mellor, 1956, Vol. 2, Suppl. 1, 592

It explodes on impact, but is less sensitive than the chlorate.

See other AMMINEMETAL OXOSALTS

4070. Mercury(II) chloride

[7487-94-7] **Cl_2Hg**



HCS 1980, 615

Hydrazine salts, Base

Hofmann, K. A. *et al., Annalen*, 1899, **305**, 191

A yellowish precipitate was obtained from the chloride and hydrazinium chlorides when basified with sodium acetate. It had N—Hg bonds and was perhaps ClHgNHNHHgCl. It exploded on heating or shock. A similar compound resulted from the bromides.

Sodium *aci*-nitromethanide

See Sodium *aci*-nitromethanide: Mercury(II) chloride

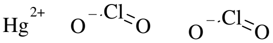
Sodium azide

See Sodium azide: Heavy metals

See other MERCURY COMPOUNDS, METAL HALIDES

4071. Mercury(II) chlorite

[73513-17-4] **Cl_2HgO_4**



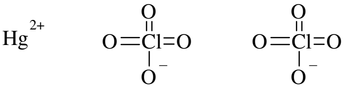
Levi, G. R., *Gazz. Chim. Ital. [2]*, 1915, **45**, 161

It is extremely unstable when dry, exploding spontaneously.

See other CHLORITE SALTS, MERCURY COMPOUNDS

4072. Mercury(II) perchlorate

[7616-83-3] **Cl_2HgO_8**



$$Hg^{2+} \quad O{=}\overset{O}{\overset{\|}{Cl}}{=}O \; | \; O^- \quad O{=}\overset{O}{\overset{\|}{Cl}}{=}O \; | \; O^-$$

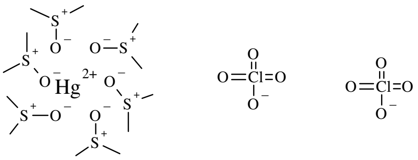
Samuels, G. J. *et al., Inorg. Chem.*, 1980, **19**, 233

A filtered solution, prepared by heating mercuric oxide with a slight excess of perchloric acid, after standing for several months precipitated a little unidentified white solid. This (but not the supernatant liquid) was very shock sensitive, and detonated as it was being rinsed out with water. (Traces of a volatile amine may have been absorbed into the acid liquor to give an amminemercury perchlorate, expected to be explosive).

See other AMMINEMETAL OXOSALTS, MERCURY COMPOUNDS, METAL PERCHLORATES

4073. Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide

[62909-81-3] (. 6DMSO) **$Cl_2HgO_8.6$ (or 4)C_2H_6OS**



1. Rayner, P. N. G., *Chem. Brit.*, 1977, **13**, 396; private comm., 1977
2. Cotton, F. A. *et al., J. Amer. Chem. Soc.*, 1960, **82**, 2886
3. Brown, A. J. *et al., J. Chem. Soc., Dalton Trans.*, 1978, 1778
4. Sandstrom, M. *et al., Acta Chem. Scand.*, 1978, **A32**, 610

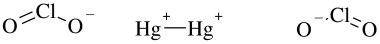
The hexasolvated compound was being prepared from a mixture of the hydrated salt, methanol and dimethyl sulfoxide but inexplicably mercury(I) oxide came out of solution. This was redissolved by addition of perchloric acid and the solution was refrigerated for 60 h. After addition of molecular sieve to remove the water present, the solution was filtered and the sieve treatment repeated four more times. During the final filtration, a violent explosion occurred in the funnel. The most likely cause was formation of methyl perchlorate promoted by the dehydrating action of the sieve, but dimethyl sulfoxide also forms an unstable salt with perchloric acid, so this also may have been involved [1]. During preparation of the hexasolvate by a published method [2], a violent explosion occurred [3]. The solid tetrasolvated product from treatment of a solution of the perchlorate in methanol—perchloric acid with DMSO at ambient temperature exploded with extreme violence after prolonged desiccation (possibly owing to formation of methyl perchlorate). Materials prepared at —78°C appeared to be free of this hazard, though they will explode under mechanical impact, etc. [4].

See Dimethyl sulfoxide: Metal oxosalts

See other METAL PERCHLORATES, MOLECULAR SIEVE INCIDENTS, SOLVATED OXOSALT INCIDENTS

4074. Mercury(I) chlorite

[101672-18-8] **$Cl_2Hg_2O_4$**



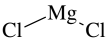
Levi, G. R., *Gazz. Chim. Ital. [2]*, 1915, **45**, 161

It is extremely unstable when dry, exploding spontaneously.

See other CHLORITE SALTS, MERCURY COMPOUNDS, REDOX COMPOUNDS

4075. Magnesium chloride

[7786-30-3] **Cl_2Mg**



Air, Mild steel, Water

1. Anon., *CISHC Chem. Safety Summ.*, 1984, **55**, 66
2. Haudt, P. R., *Mater. Perform.*, 1986, **25**(9), 49—55
3. Melcher, R. G. *et al., Am. Ind. Hyg. Assoc. J.*, 1987, **48**, 608—612

A large steel evaporator used for magnesium chloride solution was shut down for maintenance. During maintenance operations a fatality occurred from atmospheric oxygen deficiency inside the evaporator. It was found later that the oxygen content in the evaporator fell from the normal 21% to about 1% in under 24 h, and this was confirmed in laboratory tests. This was attributed to very rapid rusting of the steel under warm humid conditions in the presence of traces of magnesium chloride [1]. Further work shows that other salts (calcium bromide, calcium chloride, magnesium sulfate, potassium chloride) behave similarly, and that presence of scale is a contributory factor [2]. Magnetite scale (Fe_3O_4) on mild steel increases the depletion rate by a factor of 10, while the rust formed during the corrosion has little effect [3].

See other CORROSION INCIDENTS

Jute, Sodium nitrate

See Sodium nitrate: Jute, Magnesium chloride

See other METAL HALIDES

4076. Magnesium hypochlorite

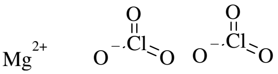
[10233-03-1] **Cl_2MgO_2**

$Mg^{2+} \quad O^{-}\text{-}Cl \quad O^{-}\text{-}Cl$

Clancey, V. J., *J. Haz. Mat.*, 1975, **1**, 83—94
The compound is very unstable, and its presence may be one of the causes of the observed explosive and apparently spontaneous decomposition of calcium hypochlorite, if produced from magnesia-containing lime (derived from dolomite).
See Chlorine: Phenylmagnesium bromide
See other METAL HYPOCHLORITES

4077. Magnesium chlorate

[10326-21-3] **Cl_2MgO_6**

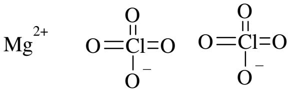


Sulfides

Mellor, 1956, Vol. 2, Suppl. 1, 584
Interaction with copper(I) sulfide is explosive, and with antimony(III) sulfide, arsenic(III) sulfide, tin(II) sulfide or tin(IV) sulfide, incandescent.
See other METAL CHLORATES

4078. Magnesium perchlorate

[10034-81-8] **Cl_2MgO_8**



$$Mg^{2+} \quad O{=}\underset{O^{-}}{\overset{O}{Cl}}{=}O \quad O{=}\underset{O^{-}}{\overset{O}{Cl}}{=}O$$

Marusch, H., *Chem. Tech.* (Berlin), 1956, **8**, 482—485
The drying agent may contain traces of perchloric acid remaining from manufacturing operations, and owing to the great desiccating power of the salt, the acid will be anhydrous. Many of the explosions experienced with magnesium perchlorate have their origins in contact of the anhydrous acid with oxidisable materials, or materials able to form unstable perchlorate esters or salts.

Alkenes

Heertjes, P. M. *et al., Chem. Weekbl.*, 1941, **38**, 85
The anhydrous salt which had been used for drying unsaturated hydrocarbons exploded on heating to 220°C for reactivation. The need to avoid contact with acidic materials is stressed. (Traces of an alkyl perchlorate may conceivably have been formed from free perchloric acid).
See Organic materials, below

Ammonia

491M, 1975, 244

Intensive drying of ammonia gas by passing it over the desiccant in a steel drying tube led to an exotherm, followed by a violent explosion. (An ammine derivative may have been formed).

See related AMMINEMETAL OXOSALTS

Argon

Dam, J. W., *Chem. Weekbl.*, 1958, **54**, 277

An explosion which occurred when argon was being dried obviously involved some (unstated) impurity in the system.

Arylhydrazine, Ether

Belcher, R., private comm., 1968

Anhydrous magnesium perchlorate was used to dry thoroughly an ethereal solution of an arylhydrazine. During evaporation of the filtered solution it exploded completely and violently. Magnesium perchlorate is rather soluble in ether and may contain traces of free perchloric acid (probably in the anhydrous form, as the magnesium salt is a powerful dehydrator). It is entirely unsuitable for drying organic solvents. (The hydrazine may have complexed with the magnesium to form a redox salt).

See related AMMINEMETAL OXOSALTS

Cellulose, Dinitrogen tetraoxide, Oxygen

Anon., *ABCM Quart. Safety Summ.*, 1961, **32**, 6

Magnesium perchlorate contained in a glass tube between wads of cotton wool was used to dry a mixture of oxygen and dinitrogen tetraoxide. After several days the drying tube exploded violently. It seems probable that the acidic fumes and cotton produced cellulose nitrate, aided by the dehydrating action of the perchlorate.

Dimethyl sulfoxide

1. Tobe, M. L. *et al., J. Chem. Soc.*, 1964, 2991
2. Anon., *Chem. Eng. News*, 1965, **43**(47), 62
3. Dessy, R. E. *et al., J. Amer. Chem. Soc.*, 1964, **86**, 28

In the preparation of anhydrous DMSO by a literature method [1], an explosion occurred during distillation from anhydrous magnesium perchlorate [2]. This may have been due to the presence of some free methanesulfonic acid as an impurity in the solvent, which could liberate traces of perchloric acid. It is known that sulfoxides react explosively with 70% perchloric acid, (but several metal perchlorates also form unstable solvates with DMSO) The alternative procedure for drying DMSO with calcium hydride [3] seems preferable, as this would also remove any acidic impurities.

See Dimethyl sulfoxide: Metal oxosalts

Ethanol

Raymond, K. R., private comm., 1983

The desiccant in a drying tube, accidentally exposed to ethanol vapour, was left for several months. The explosion which occurred when the desiccant was scraped out was certainly due to formation of ethyl perchlorate.

See related ALKYL PERCHLORATES

Ethylene oxide

491M, 1975, 314

Desiccation of gaseous ethylene oxide led to an explosion, (possibly involving formation of 2-hydroxyethyl perchlorate).

Fluorobutane, Water

Anon., *Ind. Eng. Chem. (News Ed.)*, 1939, **17**, 70

A violent explosion followed the use of magnesium perchlorate to dry wet fluorobutane. The latter was presumed to have hydrolysed to give hydrogen fluoride which had liberated perchloric acid, explosively unstable when anhydrous. (This explanation seems unlikely in view of the large disparity between dissociation constants of the two acids). Magnesium perchlorate is unsuitable for drying acidic or flammable materials; calcium sulfate would be suitable.

Organic materials

1. Hodson, R. J., *Chem. & Ind.*, 1965, 1873
2. *MCA Case History No. 243*

The use of the perchlorate as desiccant in a drybag where contamination with organic compounds is possible is considered dangerous [1]. Magnesium perchlorate ('Anhydrone') was inadvertently used instead of calcium sulfate (anhydrite) to dry an unstated reaction product before vacuum distillation. The error was realised and all solid was filtered off. Towards the end of the distillation, decomposition and an explosion occurred, possibly owing to the presence of dissolved magnesium perchlorate, or more probably to perchloric acid present as impurity in the salt [2].

Phosphorus

See Phosphorus: Magnesium perchlorate

Trimethyl phosphite

Jercinovic, L. M. *et al., J. Chem. Educ.*, 1968, **45**, 751

Contact between the salt and ester caused violent explosions on several occasions. (Methyl perchlorate may have been formed).

See other METAL PERCHLORATES

See related ALKYL PERCHLORATES

4079. Manganese(II) chloride

[7773-01-5] **Cl_2Mn**

Cl—Mn–Cl

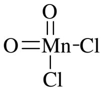
Zinc

See Zinc: Manganese dichloride

See other METAL HALIDES

4080. Manganese dichloride dioxide

[51819-69-3] **Cl_2MnO_2**



$O{=}Mn({=}O)(Cl){-}Cl$

Briggs, T. S., *J. Inorg. Nucl. Chem.*, 1968, **30**, 2867—2868

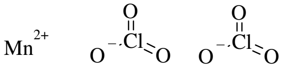
Explosively unstable if isolated as liquid at ambient temperature, it may be handled safely in carbon tetrachloride solution.

See Manganese chloride trioxide, Manganese trichloride oxide

See related METAL HALIDES, METAL OXIDES

4081. Manganese(II) chlorate

[104813-96-9] **Cl_2MnO_6**



$Mn^{2+}\ \ {}^{-}O{-}Cl({=}O){=}O\ \ {}^{-}O{-}Cl({=}O){=}O$

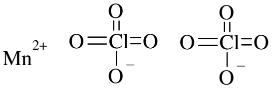
Bailar, 1973, Vol. 3, 835

The hexahydrated salt decomposes explosively above 6°C, producing chlorine dioxide.

See other METAL CHLORATES, REDOX COMPOUNDS

4082. Manganese(II) perchlorate

[13770-16-6] **Cl_2MnO_8**



$Mn^{2+}\ \ O{=}Cl({=}O)({-}O^{-}){=}O\ \ O{=}Cl({=}O)({-}O^{-}){=}O$

Sidgwick, 1950, 1285

It explodes at 195°C.

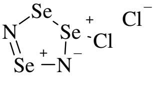
2,2-Dimethoxypropane

See 2,2-Dimethoxypropane: Metal perchlorates

See other METAL PERCHLORATES, REDOX COMPOUNDS

4083. Chloro-1,2,4-triselenadiazolium chloride (3-Chloro-1,3,4-triselenadiazolium chloride)

[ ] **$Cl_2N_2Se_3$**



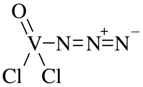
1. Chivers, T. *et al., Angew. Chem. (Int.)*, 1992, **31**(11), 1518
2. Chivers, T. *et al., Inorg. Chem.*, 1993, **32**(20), 4391

The black explosive powder previously described as Se_4N_2 is now assigned this structure. It is very sensitive when dry and handling it damp with an hydrocarbon is recommended. There is brown dimer, also explosive [2].

See related NITRIDES, NON-METAL HALIDES, N—S COMPOUNDS

4084. Vanadyl azide dichloride

[ ] **Cl_2N_3OV**

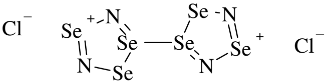


An explosive solid.

See entry METAL AZIDE HALIDES

4085. Di(triselenadiazolium) dichloride

[ ] **$Cl_2N_4Se_6$**



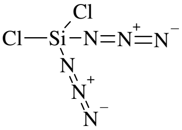
Chivers, T. *et al., Inorg. Chem.*, 1993, **32**(20), 4391

A brown explosive powder

See Chloro-1,2,4-triselenadiazolium chloride

4086. Diazidodichlorosilane

[67880-19-7] **Cl_2N_6Si**

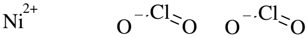


See Silicon tetraazide

See other NON-METAL AZIDES

4087. Nickel chlorite

[72248-72-7] **Cl_2NiO_4**

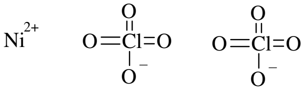


1. Mellor, 1956, Vol. 2, Suppl. 1, 574
2. Levi, G. R., *Gazz. Chim. Ital. [2]*, 1923, **53**, 245

The dihydrate explodes at 100°C [1], or on percussion, even when wet [2].

See other CHLORITE SALTS

4088. Nickel perchlorate
[13637-71-3] **Cl_2NiO_8**

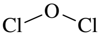


2,2-Dimethoxypropane

See 2,2-Dimethoxypropane: Metal perchlorates

See other METAL PERCHLORATES

4089. Dichlorine oxide
[7791-21-1] **Cl_2O**



1. Sidgwick, 1950, 1202
2. Jacobs, P. W. M. *et al., Chem. Rev.*, 1969, **69**, 559
3. Pilipovich, D. *et al., Inorg. Chem.*, 1972, **11**, 2190
4. Gray, P. *et al., Combust. Flame*, 1972, **18**, 361—371
5. Cady, G. H., *Inorg. Synth.*, 1957, **5**, 156

It is somewhat endothermic (ΔH_f° (g) +87.5 kJ/mol, 1.0kJ/g), the liquid may explode on pouring or sparking at 2°C, and the gas readily explodes on rapid heating or sparking [1,2], on adiabatic compression in a U-tube, or often towards the end of slow thermal decomposition. Kinetic data are summarised [3]. The spontaneously explosive decomposition of the gas was studied at 42—86°C, and induction periods up to several hours were noted [4]. Preparative precautions have been detailed [5].

See other ENDOTHERMIC COMPOUNDS, INDUCTION PERIOD INCIDENTS

Alcohols

1. Gallais, 1957, 677
2. Blau, T. E., *The Tech, (MIT)*, 1995, **115**(37)

Alcohols are oxidised explosively [1]. A moderately destructive laboratory fire was apparently initiated by reaction of the oxide with the isopropanol of a cooling bath. Details are vague, but it seems the bath had been allowed to warm, which would have pressurised, and possibly rupture, the containment of the oxide within it [2].

Carbon

Mellor, 1946, Vol. 5, 824

Addition of charcoal to the gas causes an immediate explosion, probably initiated by the heat of adsorption of the gas on the solid.

Carbon disulfide

Mellor, 1940, Vol. 6, 110

The vapours explode on contact.

Dicyanogen

Brotherton, T. K. *et al., Chem. Rev.*, 1959, **59**, 843

Contact causes ignition or explosion.

Diphenylmercury

See Diphenylmercury: Chlorine monoxide, etc.

Ethers

Gallais, 1957, 677

Ethers are oxidised explosively.

Hydrocarbons

Ip, J. K. K. *et al., Combust. Flame*, 1972, **19**, 117—129

The spontaneously explosive interaction of dichlorine oxide with methane, ethane, propane, ethylene or butadiene was investigated at 50—150°C. Self-heating occurs with ethylene, ethane and propane mixtures.

See other SELF-HEATING AND IGNITION INCIDENTS

Nitrogen oxide

Mellor, 1940, Vol. 8, 433

Interaction is explosive.

Oxidisable materials

1. Mellor, 1941, Vol. 2, 241—242; 1946, Vol. 5, 824
2. Cady, G. H., *Inorg. Synth.*, 1957, **5**, 156

The heat sensitivity (above) may explain the explosions which occur on contact of many readily oxidisable materials with this powerful oxidant. Such materials include ammonia, potassium; arsenic, antimony; sulfur, charcoal (adsorptive heating may also contribute); calcium phosphide, phosphine, phosphorus; hydrogen sulfide, antimony sulfide, barium sulfide, mercury sulfide and tin sulfide [1]. Various organic materials (paper, cork, rubber, turpentine, etc.) behave similarly [2]. Mixtures with hydrogen detonate on ignition [1].

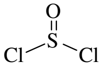
Potassium

See Potassium: Non-metal oxides

See other HALOGEN OXIDES, OXIDANTS

4090. Sulfinyl chloride (Thionyl chloride)

[7719-09-7] **Cl_2OS**



HCS 1980, 898; *RSC Lab. Hazard Data Sheet No. 26*, 1984

Cardillo, P. *Chem. Ind. (Milan)*, 1992, **74**(12), 879

Although many reactions of thionyl chloride appear endothermic, this is because the large volumes of gas evolved are doing work against atmosphere; adiabatically the situation is very different and spontanous pressurisation highly probable [Ed]. Violent reaction incidents of thionyl chloride are reviewed [1]. Many more can be found in the sub-entries below:

Ammonia MRH 0.84/16

Foote, C. S., private comm., 1965

Addition of a solution of 4-nitrobenzoyl chloride (1 g) in a large excess (10 ml) of sulfinyl chloride to ice-cold conc. ammonia solution caused a violent explosion. This may certainly be attributed to the instantaneous hydrolysis of the excess sulfinyl chloride by the aqueous ammonia with production of several l of un-neutralised acid gases in a test tube.

See Water, below

Bis(dimethylamino) sulfoxide

Armitage, D. A. *et al., J. Inorg. Nucl. Chem.*, 1974, **36**, 993

Interaction of the chloride with the sulfoxide or its higher homologues to form dialkylaminosulfinyl chlorides causes extensive decomposition, possibly explosive above 80°C.

t-Butyl methyl ether

1. Grimm, J. S. *et al., Org. Process Res. & Dev.*, 2002, **6**(6), 938
2. Editor's comment

MTBE is not recommended as a solvent for thionyl chloride reactions, due to its cleavage by hydrogen chloride producing flammable and gaseous isobutene [1]. In fact this will permit an acid catalysed reaction of the ether with thionyl chloride, giving entirely gaseous (butene, sulfur dioxide, hydrogen chloride and methyl chloride), or at least very highly volatile (butyl chloride) products, with consequent pressurisation potential [2].

Chloryl perchlorate

See Chloryl perchlorate: Thionyl chloride

1,2,3-Cyclohexanetrione trioxime, Sulfur dioxide

1. Tokura, N. *et al., Bull. Chem. Soc. Japan*, 1962, **35**, 723
2. Lewis, J. J., *J. Heterocycl. Chem.*, 1975, 12, 601

A previous method of making 4-oximino-4,5,6,7-tetrahydrobenzofurazan by cyclising the oxime with sulfinyl chloride in liquid sulfur dioxide sometimes led to explosive reactions [1]. A new procedure involving aqueous calcium carbonate is quite safe [2].

Diisopropyl malonate

McKeown, R. H., private comm., 1985

During reflux of a mixture to produce malonoyl chloride, vivid sparks were seen in the flask, and the reaction was closed down without mishap. No explanation is apparent, but the diisopropyl ester structure appears likely to be susceptible to autoxidation on storage, and peroxides may possibly have been involved in the phenomenon.

See related PEROXIDATION INCIDENTS

Dimethyl sulfoxide

See Dimethyl sulfoxide: Acyl halides

Dimethylformamide

1. Spitulnik, M. J., *Chem. Eng. News*, 1977, **55**(31), 31
2. Joshi, M. S., *Chem. Eng. News*, 1986, **64**(14), 2
3. Zemlicka, J., *Chem. Eng. News*, 1986, **64**(25), 4

Some 200 kg of a mixture of sulfinyl chloride and DMF decomposed vigorously after storage for several h at ambient temperature. This was attributed to the presence of 90 ppm each of iron and zinc in the chloride used for the preparation. Mixtures of the pure components remained unchanged for 48 h, but addition of 200 ppm of iron powder led to exothermic decomposition after stirring for 22 h [1]. During vacuum removal of sulfur dioxide from the reaction mixture in preparation of *N,N*-dimethylchloromethyliminium chloride, a sudden exotherm and pressure increase occurred in a 400 l reactor. Study of the reaction in an adiabatic calorimeter showed that a runaway reaction developed within 8 h at 60°C, or within 20 min at 85°C at ambient pressure. Reaction slurry from which part of the sulfur dioxide had been removed decomposed even more rapidly [2]. The use of phosgene in the reaction in place of sulfinyl chloride gives a more controlled reaction which does not need heating [3].

See Dimethylformamide: Halocarbons, etc.

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

Esters, Metals

1. Spagnolo, C. J. *et al., Chem. Eng. News*, 1992, **70**(22), 2
2. Wang, S. S. Y. *et al., Process Safety Progr.,* 1994, **13**(3), 153

It was found that a solution of thionyl chloride in ethyl acetate burst galvanised drums on storage. Further investigation demonstrated an exothermic gas-evolving reaction between the ester and the chloride, initiated by iron or zinc, to give chloroethane, acetyl chloride and sulfur dioxide. A similar reaction is sometimes used synthetically on lactones with Lewis acid catalysis, especially zinc chloride. This is therefore probably a general ester reaction [1]. A more comprehensive, but scarcely more comprehending, study of the ethyl acetate/thionyl chloride reaction demonstrates involvement of zinc. Elemental sulphur is apparently among the products [2].

See Diisopropyl malonate (above)

See Propionoyl chloride: Diisopropyl ether

See Sulfonyl chloride: Organic materials, metals

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

Heterocyclic amines

See HETEROCYCLIC*N*-SULFINYLAMINES

Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

Linseed oil, Quinoline MRH Quinoline 1.63/99+

1. Fieser, L. F. *et al., Org. Synth.*, 1943, Coll. Vol. 2, 570
2. Laws, G. F., private comm., 1966

It is important to add the quinoline and linseed oil, used in purifying the chloride [1], to the chloride. If reversed addition is used, a vigorous decomposition may occur [2].

Lithium

See Lithium: Sulfinyl chloride

Other reactants

Yoshida, 1980, 57

MRH values calculated for 14 combinations with various reagents are given.

Sodium MRH 5.27/33

See Sodium: Non-metal halides

Tetrahydrofuran

Jackson, R. W. *et al., Chem. Eng. News*, 1988, **66**(27), 2

Unstirred mixtures of sulfinyl chloride and tetrahydrofuran may react extremely exothermally and with gas evolution when heated to 60°C, the products of ring-scission being bis(4-chlorobutyl) ether, 1,4-dichlorobutane and sulfur dioxide. Some ratios of the two reactants enhance the tendency, and relatively confined mixtures may explode. Sufficient heat to initiate the reaction may arise from self-mixing of the layered liquids, the chloride being twice as dense as THF.

See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS

Toluene, Ethanol, Water

Anon., *Univ. Safety Assoc., Safety Newsletter*, 1982—1984

A solution of the chloride (120 ml) in toluene (750 ml) was treated (apparently without effective stirring) with excess sodium bicarbonate solution to destroy it. When reaction had ceased, the organic layer was poured into a waste solvent drum. Vigorous evolution of sulfur dioxide and hydrogen chloride then ensued from reaction with ethanol (toluene-soluble) in the waste drum. For destruction of solutions of sulfinyl chloride in water-insoluble solvents, extremely good agitation is necessary to ensure proper contact with a basic reagent. Ammonia is more soluble in toluene than is water, so ammonia solution should be used after bicarbonate treatment to ensure complete destruction.

Water

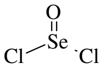
MCA Case History No. 1808

Passage of thionyl chloride through a flexible metal transfer hose which was contaminated with water or sodium hydroxide solution caused the hose to burst. Interaction with water violently decomposes the chloride to hydrogen chloride (2 mol) and sulfur dioxide (1 mol), the total expansion ratio from liquid to gas being 993:1 at 20°C, so very high pressures may be generated.

See other ACYL HALIDES, NON-METAL HALIDES

4091. Seleninyl chloride

[7791-23-3] **Cl_2OSe**



Antimony

Mellor, 1947, Vol. 10, 906

Powdered antimony ignites on contact with the chloride.

Metal oxides

Mellor, 1947, Vol. 10, 909

In contact with silver oxide, light is evolved and sufficient heat to decompose some of it. Similar effects were observed with lead(II) oxide, lead(IV) oxide and lead (II)(IV) oxide.

Phosphorus

Mellor, 1947, Vol. 10, 906

Red phosphorus evolves light and heat in contact with the chloride, while white phosphorus explodes.

See other NON-METAL HALIDES

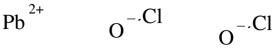
Potassium

Mellor, 1947, Vol. 10, 908

Potassium explodes violently in contact with the liquid.

4092. Lead(II) hypochlorite

[ ] **Cl_2O_2Pb**



Hydrogen sulfide

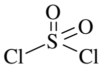
Pascal, 1960, Vol. 13.1, 1004

Ignition occurs on contact.

See other METAL HYPOCHLORITES

4093. Sulfonyl chloride (Sulfuryl chloride)

[7791-25-5] **Cl_2O_2S**



Alkalies

Brauer, 1963, Vol. 1, 385

Reaction with alkalies may be explosively violent.

Diethyl ether

Dunstan, I. *et al., Chem. & Ind.*, 1966, 73

A solution of sulfuryl chloride in ether vigorously decomposed, evolving hydrogen chloride. This was shown to be accelerated by the presence of peroxides. Peroxide-free ether should be used, and with care.

Dimethyl sulfoxide

See Dimethyl sulfoxide: Acyl halides

Dinitrogen pentaoxide

See Dinitrogen pentaoxide: Sulfur dichloride, etc.

Lead dioxide

See Lead(IV) oxide: Non-metal halides

Organic materials, Metals

Anon., personal communication, 1996

Waste ethyl acetate containing sulfuryl chloride and thionyl chloride was stored in a galvanised steel drum. This later burst, although sulfuryl chloride is supplied in such drums they are unsafe with contaminants. The material can chlorinate many active organics, including aromatics, ketones and probably esters. This will release sulphur dioxide and hydrogen chloride, a fairly soluble gas, which will react with zinc and iron to produce hydrogen, an insoluble gas, and zinc or iron chlorides, both catalysts for many reactions including ester cleavage.

See Sulfinyl chloride: Esters, Metals

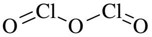
Phosphorus

See Phosphorus: Non-metal halides

See other ACYL HALIDES, NON-METAL HALIDES

4094. Dichlorine trioxide

[17496-59-2] **Cl_2O_3**



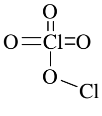
1. McHale, E. T. *et al., J. Amer. Chem. Soc.*, 1967, **89**, 2796
2. McHale, E. T. *et al., J. Phys. Chem.*, 1968, **72**, 1849—1856

It is endothermic (ΔH_f° (g) + 76.2 kJ/mol, 0.64 kJ/g), very unstable, and the vapour explodes at about 2 mbar and well below 0°C [1]. It has been identified as the intermediate involved in the delayed explosion of chlorine dioxide [2].

See other ENDOTHERMIC COMPOUNDS, HALOGEN OXIDES

4095. Chlorine perchlorate

[27218-16-2] **Cl_2O_4**



1. Schack, C. J. *et al., Inorg. Chem.*, 1970, **9**, 1387
2. Schack, C. J. *et al., Inorg. Chem.*, 1971, **10**, 1078

A shock-sensitive explosive compound [1]. Bromine perchlorate is also unstable [2].

Chlorotrifluoroethylene

Schack, C. J. *et al., Inorg. Chem.*, 1973, **12**, 897

Interaction of the reactants (pre-mixed at —196°C) during warming to —78°, then ambient temperature, exploded. Progressive addition of the alkene to the perchlorate at —78° was uneventful.

Perfluoroalkyl iodides

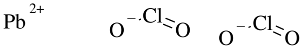
Schack, C. J. *et al., Inorg. Chem.*, 1975, **14**, 145—151

Reaction mixtures of chlorine perchlorate with perfluoromethyl iodide, 1,2-diiodoperfluoroethane or 1,3-diiodoperfluoropropane occasionally deflagrated at or below ambient temperature.

See other HALOGEN OXIDES

4096. Lead(II) chlorite

[13453-57-1] **Cl_2O_4Pb**



Alone, or Antimony sulfide, or Sulfur

Mellor, 1941, Vol. 2, 283

It explodes on heating above 100°C or on rubbing with antimony sulfide or fine sulfur.

Non-metals

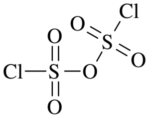
Pascal, 1960, Vol. 16, 264

Carbon, red phosphorus, or sulfur are oxidised violently by the chlorite.

See other CHLORITE SALTS, METAL OXOHALOGENATES

4097. Disulfuryl dichloride

[7791-27-7] **$Cl_2O_5S_2$**



Phosphorus

See Phosphorus: Non-metal halides

Water

Sveda, M., *Inorg. Synth.*, 1950, **3**, 127

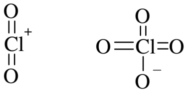
The pure acid chloride reacts slowly with water, but if more than a few % of chlorosulfuric acid (a usual impurity) is present, the reaction is rapid and could become violent with large quantities.

See other ACYL HALIDES, NON-METAL HALIDES (AND THEIR OXIDES)

See related ACID ANHYDRIDES

4098. Chloryl perchlorate

[12442-63-6] **Cl_2O_6**



The value of the heat of formation quoted for the monomeric form, chlorine trioxide, indicates considerable endothermicity; (ΔH_f° (g) +154.8 kJ/mol, 1.85 kJ/g).

Organic matter, or Water

1. Mellor, 1956, Vol. 2, Suppl. 1, 539
2. Wechsberg, M. *et al., Inorg. Chem.*, 1972, **11**, 3066
3. Sorbe, 1968, 45
4. Pascal, J. L. *et al., J. Chem. Soc., Dalton Trans.*, 1985, 297

Though the least explosive of the chlorine oxides, being insensitive to heat or shock, it is a very powerful oxidant and needs careful handling. It violently or explosively oxidises ethanol, stopcock grease, wood and organic matter generally, and explodes on contact with water [1]. It explodes on heating [2], and explosions in contact with organic matter below —70°C have been reported [3]. A later reference indicates that it is shock-sensitive, however [4], and stresses the need for care in its use as a most effective perchlorylating agent.

Tetrachlorosilane, or Tetrabromosilane

Schmeisser, M., *Angew. Chem.*, 1955, **67**, 499

Reaction gives explosive solids, apparently perchloratosiloxanes.

See Tetraperchloratosilicon

Thionyl chloride

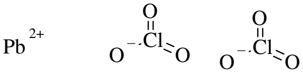
Schmeisser, M. *Angew. Chem.*, 1955, **67**, 499

It is liable to explode on contact with thionyl chloride in absence of inert solvent.

See other ENDOTHERMIC COMPOUNDS, HALOGEN OXIDES, OXIDANTS

4099. Lead(II) chlorate

[10294-47-0] **Cl_2O_6Pb**

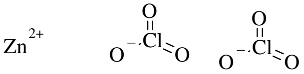


Bailar, 1973, Vol. 2, 130

Thermal decomposition may be explosive.

See other METAL CHLORATES

4100. Zinc chlorate
[10361-95-2] **Cl_2O_6Zn**



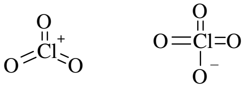
Sorbe, 1968, 158
The tetrahydrated salt decomposes explosively at 60°C.

Other reactants
Yoshida, 1980, 63—64
MRH values calculated for 30 combinations with oxidisable materials are given.

Sulfides MRH values below reference
Mellor, 1956, Vol. 2, Suppl. 1, 584
MRH Copper(II) sulfide 2.84/38, antimony(III) sulfide 2.89/41, tin(II) sulfide 3.05/43, tin(IV) sulfide 3.1/37

Interaction with copper(II) sulfide is explosive, and incandescent with antimony(III) sulfide, arsenic(III) sulfide, tin(II) sulfide and tin(IV) sulfide.
See other METAL CHLORATES

4101. Perchloryl perchlorate (Dichlorine heptaoxide)
[10294-48-1] **Cl_2O_7**



1. Mellor, 1956, Vol. 2, Suppl. 1, 542
2. Schmeisser, M., *Angew. Chem.*, 1955, **67**, 498

It is rather endothermic (ΔH_f° (g) +265.3 kJ/mol, 1.45 kJ/g) and explodes violently on impact or rapid heating, but is a less powerful oxidant than other chlorine oxides [1]. It is now formulated as perchloryl perchlorate [2].

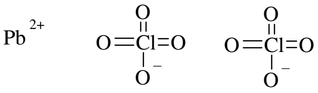
Bromine pentafluoride
Lawless, 1968, 173
Mixtures are shock-sensitive explosives.

Copper phthalocyanine
Osadchaya, L. I. *et al., Chem. Abs.*, 1997, **126**, 309255v
A shock-sensitive explosive complex is formed, which could not be characterised.

Iodine
Kirk-Othmer, 1964, Vol. 5, 5
Explosion on contact.
See other ENDOTHERMIC COMPOUNDS, HALOGEN OXIDES

4102. Lead perchlorate

[13637-76-8] **Cl_2O_8Pb**



$$Pb^{2+} \quad O=\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{Cl}}}=O \quad O=\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{Cl}}}=O$$

Methanol

Willard, H. H. *et al., J. Amer. Chem. Soc.*, 1930, **52**, 2396

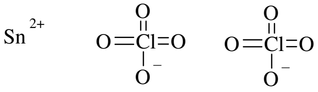
A saturated solution of anhydrous lead perchlorate in dry methanol exploded violently when disturbed. Methyl perchlorate may have been involved.

See ALKYL PERCHLORATES

See other METAL PERCHLORATES

4103. Tin(II) perchlorate

[25253-54-7] **Cl_2O_8Sn**



$$Sn^{2+} \quad O=\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{Cl}}}=O \quad O=\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{Cl}}}=O$$

Bailar, 1973, Vol. 2, 76

The trihydrated salt decomposes explosively at 250°C.

Aromatic Schiff bases

Dwivedi, B. K. *et al., Indian J. Chem.*, 1987, **26A**, 618—620

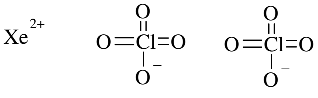
Twelve tris-complexes $[Sn(ClO_4)_2 \cdot 3L]$ between tin(II) perchlorate and Schiff bases derived from salicylaldehyde, anisaldehyde, or 2-hydroxy-1-naphthaldehyde and aromatic amines were investigated for thermal instability.

See other METAL PERCHLORATES, REDOX COMPOUNDS

See related AMMINEMETAL OXOSALTS

4104. Xenon(II) perchlorate (Bis(perchloryloxy)xenon)

[25523-79-9] **Cl_2O_8Xe**



$$Xe^{2+} \quad O=\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{Cl}}}=O \quad O=\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{Cl}}}=O$$

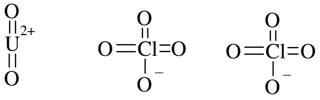
1. Wechsberg, M. *et al., Inorg. Chem.*, 1972, **11**, 3066
2. Kirk Othmer, 1980, **Vol 12**, 293

During preparation from perchloric acid and xenon difluoride at —50°C, violent explosions occurred if the reaction mixture was allowed to warm up rapidly [1]. Detonates easily and should be handled with extreme care [2].

See other NON-METAL PERCHLORATES, XENON COMPOUNDS

4105. Uranyl perchlorate

[13093-00-0] **$Cl_2O_{10}U$**



Ethanol

Erametsa, O., *Suomen Kemist*, 1942, **15B**, 1

Attempted recrystallisation of the salt from ethanol caused an explosion (probably involving ethyl perchlorate).

See ALKYL PERCHLORATES

See other METAL PERCHLORATES

4106. Lead chloride

[7758-95-4] **Cl_2Pb**

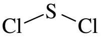
Calcium

See Calcium: Lead chloride

See other METAL HALIDES

4107. Sulfur dichloride

[10545-99-0] **Cl_2S**



(*MCA SD-77*, 1960); *HCS 1980*, 875

Acetone

Fawcett, F. S. *et al., Inorg. Synth.*, 1963, **7**, 121

Acetone is an effective solvent for cleaning traces of sulfur chlorides from reaction vessels, but care is necessary, as the reaction is vigorous if more than a trace is present.

Dimethyl sulfoxide

See Dimethyl sulfoxide: Acyl halides, etc.

Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

Metals

See Potassium: Non-metal halides, *and* Sodium: Non-metal halides

Oxidants

See Dinitrogen pentaoxide: Sulfur dichloride

Nitric acid: Sulfur halides

Perchloryl fluoride: Hydrocarbons, etc.

Toluene

1. Caporossi, J. C., *Chem. Eng. News*, 1988, **66**(32), 2
2. Author's comments, 1988
3. Urben, P. G., private comm., 1989

Toluene was added to a closed mild steel storage tank containing sulfur dichloride, and the vessel was subsequently ruptured by overpressurisation. It was later found that the exothermic reaction between toluene and sulfur dichloride was catalysed by iron or iron(III) chloride [1]. Several reactions may have been involved in this chlorination system, many capable of iron catalysis arising from the inevitable formation of traces of iron(III) chloride from contact of sulfur dichloride with mild steel. Initially at low temperatures, exothermic formation of 2- and 4-chlorotoluene with evolution of hydrogen chloride and formation of more iron(III) chloride would occur. As the temperature and concentration of catalyst rose, side-chain chlorination would set in, leading to formation of chloromethyl-, dichloromethyl- and trichloromethyl-benzenes and much more heat and hydrogen chloride. The direct catalysed reaction of toluene with sulfur dichloride to form toluenesulfenyl chloride could also occur [2], with the subsequent possibility of oxidation to the disulfide [3]. It is also known that chloromethylbenzene (benzyl chloride) will undergo a Friedel-Crafts self-condensation reaction, catalysed by iron(III) chloride, to form polybenzyls. Both of these reactions would again liberate hydrogen chloride. With so many possibilities for evolution of hydrogen chloride gas, it is perhaps not surprising that the mild steel vessel ruptured [2].

See Benzyl chloride: Catalytic impurities

Water

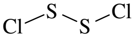
MCA SD-77, 1960

Exothermic reaction with water or steam.

See other NON-METAL HALIDES

4108. Disulfur dichloride

[10025-67-9] **Cl_2S_2**



(*MCA SD-77*, 1960); *HCS 1980*, 874

Aluminium

See Aluminium: Non-metal halides

Antimony, or Antimony sulfide, or Arsenic sulfide

Mellor, 1947, Vol. 10, 641

Interaction at ambient temperature is surprisingly energetic.

Chromyl chloride

See Chromyl chloride: Non-metal halides

Dimethyl sulfoxide

See Dimethyl sulfoxide: Acyl halides, etc.

Mercury oxide

Mellor, 1947, Vol. 10, 643

Interaction is rapid and very exothermic.

Phosphorus(III) oxide

See Tetraphosphorus decaoxide: Disulfur dichloride

Potassium

Mellor, 1947, Vol. 10, 642

A mixture of potassium and the liquid chloride is shock-sensitive and explodes violently on heating.

Sodium peroxide

See Sodium peroxide: Non-metal halides

Tin

Pascal, 1963, Vol. 8.3, 309

Interaction is violent.

Unsaturated materials

1. Mellor, 1947, Vol. 10, 64—642
2. Huestis, B. L., *Safety Eng.*, 1927, **54**, 95

Alkenes, terpenes and unsaturated glycerides react exothermically, some vigorously [1]. Ignition may occur with some organic materials [2].

Water

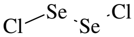
MCA SD-77, 1960

As with sulfinyl chloride, the exothermic reaction with limited amounts of water may be dangerously violent under confinement because of rapid gas evolution.

See other GAS EVOLUTION INCIDENTS, NON-METAL HALIDES

4109. Diselenium dichloride

[10025-68-0] **Cl_2Se_2**



Alkali metals or oxides

See Potassium: Non-metal halides
Potassium dioxide: Diselenium dichloride
Sodium peroxide: Non-metal halides
Sodium: Non-metal halides

Aluminium

See Aluminium: Non-metal halides

Trimethylsilyl azide

See Trimethylsilyl azide: Selenium halides

See other NON-METAL HALIDES

4110. Tin(II) chloride

[7772-99-8] **Cl_2Sn**

Cl—Sn—Cl

HCS 1980, 900

Bromine trifluoride
See Bromine trifluoride: Tin(II) chloride

Calcium acetylide MRH 1.51/25
See Calcium acetylide: Tin(II) chloride

Hydrazine
Mellor, 1941, Vol. 7, 430
Stannous chloride reacts with hydrazine in ethanol to give a precipitate, believed the dihydrazino adduct, which explodes on heating.

Hydrogen peroxide MRH 1.21/15
See Hydrogen peroxide: Tin(II) chloride

Metal nitrates MRH Ammonium nitrate 1.21/30
See METAL NITRATES: Esters, etc.

Other reactants
Yoshida, 1980, 56
MRH values calculated for 16 combinations, largely with oxidants, are given.
See other METAL HALIDES, REDUCANTS

4111. Titanium(II) chloride

[10049-06-6] **Cl_2Ti**

Cl—Ti—Cl

1. Mellor, 1941. Vol. 7, 75
2. Brauer, 1965, Vol. 2, 1187
3. *NSC Data Sheet 485*, 1966

It readily ignites in air, particularly if moist [1,2]. The dichloride on heating under inert atmospheres disproportionates into the tetrachloride and pyrophoric titanium [3].

Water
Gallais, 1957, 431
Interaction at ambient temperature is violent, and water is reduced with evolution of hydrogen.
See other METAL HALIDES, REDUCANTS

4112. Vanadium dichloride

[10580-52-6] **Cl_2V**

Cl—V—Cl

Platinum, Water

Ephraim, 1954, 261

Vanadium(II) chloride dissolved in water is slowly oxidised by the solvent with evolution of hydrogen. Contact with platinum foil accelerates the reaction to violence.

See other METAL HALIDES, REDUCANTS

4113. Tungsten dichloride

[13470-12-7] **Cl_2W**

Cl—W—Cl

Preparative hazard

Mussell, R. D. *et al., Inorg. Chem.*, 1990, **29**(19), 3711

Explosions sometimes resulted on opening sealed tubes in which complex mixed chloride salts of this compound had been prepared. There is no obvious source of pressure in the reaction mixture of tungsten hexachloride, sodium and aluminium chlorides and aluminium metal.

See other METAL HALIDES, REDUCANTS

4114. Zinc chloride

[7646-85-7] **Cl_2Zn**

Cl—Zn—Cl

HCS 1980, 965

Zinc

See Zinc: Zinc chloride

See other METAL HALIDES

4115. Zirconium(II) chloride

[13762-26-0] **Cl_2Zr**

Cl—Zr—Cl

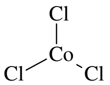
Sidgwick, 1950, 652

When warm it ignites in air.

See other METAL HALIDES, REDUCANTS

4116. Cobalt(III) chloride

[10241-04-0] **Cl_3Co**



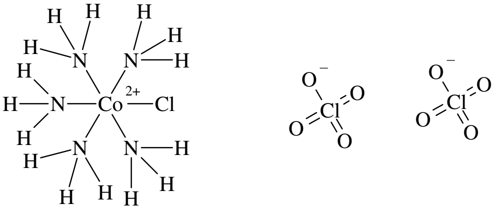
Pentacarbonyliron, Zinc

See Pentacarbonyliron: Transition metal halides, etc.

See other METAL HALIDES

4117. Pentaamminechlorocobalt(III) perchlorate

[15156-18-0] **$Cl_3CoH_{15}N_5O_8$**

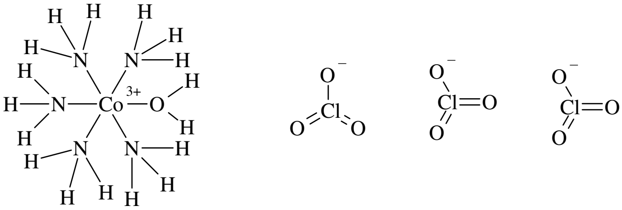


Explodes at 320°C; high impact sensitivity.

See entry AMMINEMETAL OXOSALTS

4118. Pentaammineaquacobalt(III) chlorate

[13820-81-0] **$Cl_3CoH_{17}N_5O_{10}$**



Salvadori, R., *Gazz. Chim. Ital. [2]*, 1910, **40**, 9

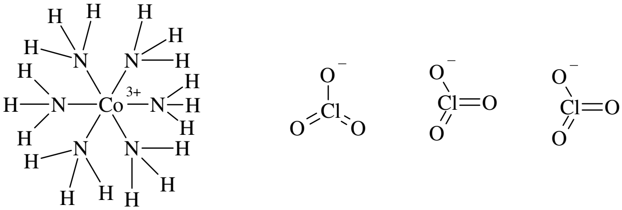
It is of zero oxygen balance and explodes on impact, or heating to 130°C.

See entry OXYGEN BALANCE

See other AMMINEMETAL OXOSALTS

4119. Hexaamminecobalt(III) chlorate

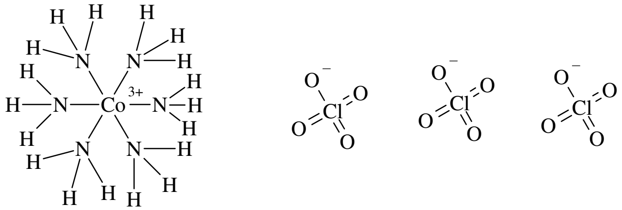
[26156-56-9] **$Cl_3CoH_{18}N_6O_9$**



Friederich, W. *et al., Z. Ges. Schiess-Sprengstoffw.*, 1926, **21**, 49

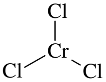
The complex salt is explosive.
See other AMMINEMETAL OXOSALTS

4120. Hexaamminecobalt(III) perchlorate
[13820-83-2] **$Cl_3CoH_{18}N_6O_{12}$**



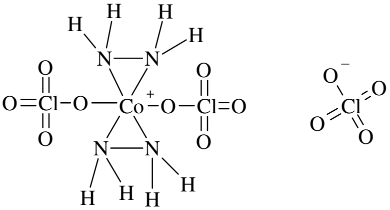
It explodes at 360°C, is highly impact-sensitive and has +14.2% oxygen balance.
See entry AMMINEMETAL OXOSALTS, OXYGEN BALANCE

4121. Chromium(III) chloride
[10025-73-7] **Cl_3Cr**



Lithium, Nitrogen
See Lithium: Metal chlorides, etc.
See other METAL HALIDES

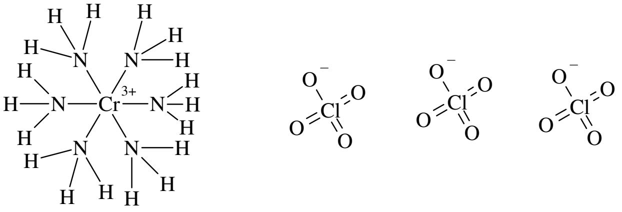
4122. Bis(hydrazine)diperchloratochromium(III) perchlorate
[73411-45-7] **$Cl_3CrH_8N_4O_{12}$**



Patil, K. C. *et al., Chem. & Ind.*, 1979, 902
It ignites at 240°C in air and decomposes explosively, but surprisingly is not sensitive to friction or impact, unlike its nickel analogue. It shows +118% oxygen balance.
See entry REDOX COMPOUNDS
See other AMMINEMETAL OXOSALTS, OXYGEN BALANCE

4123. Hexaamminechromium(III) perchlorate

[15203-80-2] **$Cl_3CrH_{18}N_6O_{12}$**



Ethanol, Ether

1. Pennington, D. E., *Chem. Eng. News*, 1982, **60**(33), 55
2. Cartwright, R. V., *Chem. Eng. News*, 1983, **61**(6), 4

A second crop of material (+14.2% oxygen balance), precipitated by addition of excess perchloric acid to the liquor, was collected on a sinter, washed and dried with ethanol, then ether. Stirring the filter cake led to a violent explosion [1]: formation of ethyl perchlorate seems to have been the most likely cause. The advantages of using plastic sintered funnels in reducing friction and the extent of fragmentation if an explosion occurs were stressed later [2].

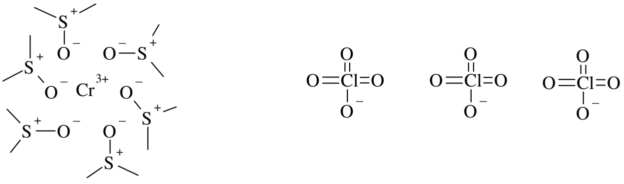
See ALKYL PERCHLORATES

See entry OXYGEN BALANCE

See other AMMINEMETAL OXOSALTS, FRICTIONAL INITIATION INCIDENTS

4124. Chromium(III) perchlorate . 6dimethyl sulfoxide

[59675-70-6] **$Cl_3Cr.6C_2H_6OS$**



Langford, C. H. *et al., J. Chem. Soc., Chem. Comm.*, 1977, 139

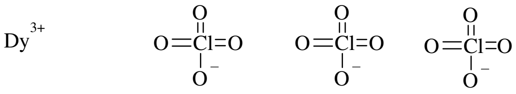
The hexasolvated complex may be hazardous with respect to detonation. Other metal perchlorates and nitrates solvated with DMSO are explosive.

See Dimethyl sulfoxide: Metal oxosalts

See other METAL PERCHLORATES, SOLVATED OXOSALT INCIDENTS

4125. Dysprosium perchlorate

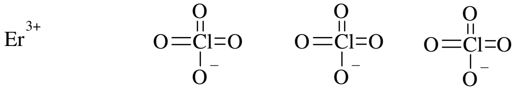
[14017-53-9] **Cl_3DyO_{12}**



Birnbaum, E. R. *et al., Inorg. Chem.*, 1973, **12**, 379

The anhydrous salt was stable to 300°C or to impact of a steel hammer, but a mild explosion occurred when a grease-containing sample was disturbed with a metal spatula.
See other FRICTIONAL INITIATION INCIDENTS, METAL PERCHLORATES

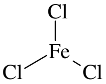
4126. Erbium perchlorate
[14017-55-1] **Cl_3ErO_{12}**



Acetonitrile

Wolsey, W. C., *J. Chem. Educ.*, 1973, **50**(6), A336—337
The shock-sensitive glassy residue (containing traces of acetonitrile), left after heating the tetrasolvated salt to above 150°C on a vacuum line, exploded violently when scraped with a spatula. (Oxygen balance of salt +700%).
See other FRICTIONAL INITIATION INCIDENTS, METAL PERCHLORATES, SOLVATED OXOSALT INCIDENTS

4127. Iron(III) chloride
[7705-08-0] **Cl_3Fe**



HCS 1980, 501

Aluminium

Anon., University of Delaware Occupational Health and Safety, www.udel.edu/OHS/ferrichloride
An incident is reported in which ferric chloride reacted violently with an aluminium dish being used as a reaction vessel. This is the halide variant of the classic Thermite reaction.
See Metals, below
See other THERMITE REACTIONS

Chlorine, Monomers

See Chlorine: Iron(III) chloride, Monomers

Ethylene oxide

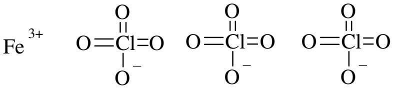
See Ethylene oxide: Contaminants

Metals

See Potassium: Metal halides
Sodium: Metal halides
See other METAL HALIDES

4128. Iron(III) perchlorate

[13537-24-1] **Cl_3FeO_{12}**



Acetonitrile

Bancroft, G. M. *et al., Can. J. Chem.*, 1974, **52**, 783

The violent reaction which occurred on dissolution of the anhydrous salt in acetonitrile did not occur with the hydrated salt.

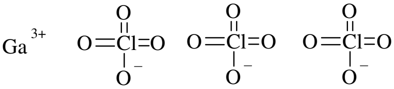
Dimethyl sulfoxide

See Dimethyl sulfoxide: Metal oxosalts

See other METAL PERCHLORATES, SOLVATED OXOSALT INCIDENTS

4129. Gallium perchlorate

[17835-81-3] **Cl_3GaO_{12}**



1. Foster, L. S., *J. Amer. Chem. Soc.*, 1933, **61**, 3123
2. Foster, L. S., *Inorg. Synth.*, 1946, **2**, 28

During preparation by dissolving the metal in 72% perchloric acid, the hexahydrate separates as a crystalline solid. After filtration, the damp crystals must not contact any organic material (filter paper, horn spatula, or recrystallisation solvent) as the adherent perchloric acid is above 72% concentration owing to the hexahydrate formation [1,2].

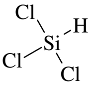
See Perchloric acid: Dehydrating agents

See other METAL PERCHLORATES

See related SOLVATED OXOSALT INCIDENTS

†4130. Trichlorosilane

[10025-78-2] **Cl_3HSi**



HCS 1980, 924

1. Müller, R. *et al., J. Prakt. Chem.*, 1966, **31**, 1—6
2. Britton, L. G., *Plant/Oper. Progr.*, **9**(1), 16

The pure material is not impact-ignitable in absence of electrostatic charges, but technical material (possibly containing dichlorosilane) is [1]. Hazards are reviewed and an Ait of 182°C established [2].
See other STATIC INITIATION INCIDENTS

Acetonitrile, Diphenyl sulfoxide

Benkeser, R. A., *Chem. Eng. News*, 1978, **56**(32), 107

Use of a single portion of trichlorosilane added to acetonitrile at 10°C to reduce diphenyl sulfoxide led to a violent explosion. The reaction previously had been effected uneventfully in a wide range of other solvents. The explosion was attributed to use of acetonitrile as solvent and/or the addition of the trichlorosilane as a single portion.

Other reactants

Yoshida, 1980, 252

MRH values calculated for 13 combinations with oxidants are given.

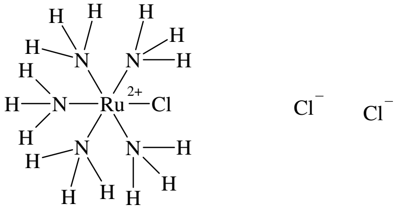
Styrene

Anon., *Chem. Eng. News*, 1994, **72**(26), 6

A drum of these two, apparently freshly mixed as feed for a reaction, pressurised and exploded. The subsequent fire destroyed the plant and injured 31 people. Styrene is polymerisable and the two probably react by Friedel-Crafts type chemistry, if suitably catalysed. It is not reported whether the drum was lined, plain steel, or galvanised.
See other HALOSILANES

4131. Pentaamminechlororuthenium chloride

[18532-87-1] **$Cl_3H_{15}N_5Ru$**



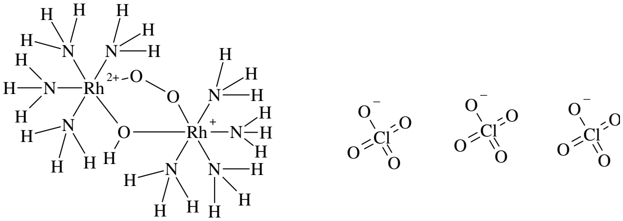
Sodium azide

Allen, A. D. *et al., Inorg. Synth.*, 1970, **12**, 5—6

During treatment with sodium azide of an intermediate (believed to be pentaammineaquaruthenium(III) derived from the title compound) to produce pentaamminedinitrogenruthenium(II) solutions, a dangerously explosive red solid may be produced. The solid, pentaammineazidoruthenium(III) will, however, decompose on standing to give the desired dinitrogen species.
See Hydrazine: Ruthenium(III) chloride
See other AMMINEMETAL HALIDES
See related METAL HALIDES

4132. Octaammine-μ-hydroxy[μ-(peroxy-*O:O'*)]dirhodium(3+) perchlorate

[113728-41-9] **$Cl_3H_{25}N_8O_{15}Rh_2$**



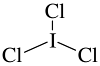
Springborg, J. *et al., Acta Chem. Scand. Sec. A*, 1987, **A41**, 485

The complex may detonate when subjected to mechanical shock.

See other AMMINEMETAL OXOSALTS

4133. Iodine trichloride

[865-44-1] **Cl_3I**



Phosphorus

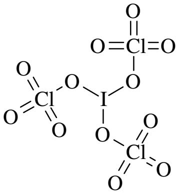
Pascal, 1960, Vol. 16.1, 578

Phosphorus ignites on contact with iodine trichloride.

See other INTERHALOGENS

4134. Iodine(III) perchlorate

[38005-31-1] **Cl_3IO_{12}**



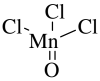
Christe, K. O. *et al., Inorg. Chem.*, 1972, **11**, 1683

The solid was stable at —45°C but exploded on laser irradiation at low temperature.

See other IODINE COMPOUNDS, IRRADIATION DECOMPOSITION INCIDENTS, NON-METAL PERCHLORATES

4135. Manganese trichloride oxide

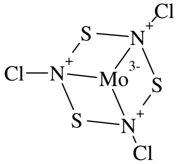
[23097-77-0] **Cl_3MnO**



Briggs, T. S., *J. Inorg. Nucl. Chem.*, 1968, **30**, 2867—2868
Explosively unstable if isolated as a liquid at ambient temperature, it may be handled safely in carbon tetrachloride solution.
See Manganese chloride trioxide, Manganese dichloride dioxide
See related METAL HALIDES, METAL OXIDES

4136. 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum

[ ] **$Cl_3MoN_3S_3$**

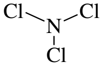


Water

Wynne, K. J. *et al., J. Inorg. Nucl. Chem.*, 1968, **30**, 2851
A 2 g quantity of the product of interaction of hexacarbonylmolybdenum and thiazyl chloride, possibly constituted as shown, reacted explosively with water.
See other N-HALOGEN COMPOUNDS, N—S COMPOUNDS

4137. Nitrogen trichloride (Trichloramine)

[10025-85-1] **Cl_3N**



HCS 1980, 686

1. Mellor, 1940, Vol. 8, 598—604; 1967, Vol. 8, Suppl. 2.2, 411
2. Sidgwick, 1950, 705
3. Anon., *ABCM Quart. Safety Summ.*, 1946, **17**, 17
4. Brauer, 1963, Vol. 1, 479
5. Schlessinger, G. G., *Chem. Eng. News*, 1966, **44**(33), 46
6. Kovacic, P. *et al., Org. Synth.*, 1968, **48**, 46
7. Dokter, T., private comm., 1985
8. Dokter, T., *J. Haz. Mat.*, 1985, **10**, 205—222
9. Cardillo. P., *J. Loss Prev. Proc. Ind.*, 2000, **14**, 69
10. Gustin, J.-L., *Chem. Health & Safety*, 2005, **12**(1), 5

Contact above 0°C of excess chlorine or a chlorinating agent with aqueous ammonia, ammonium salts or a compound containing a hydrolysable amino-derivative, or electrolysis of ammonium chloride solution produces the highly endothermic (ΔH_f° (g) +230.1 kJ/mol, 1.91 kJ/g) and explosive nitrogen trichloride as a water-insoluble yellow oil [1,2,3]. Detonation at constant volume generates 5,500 Bar maximum pressure and 2,100°C maximum temperature. As a vapour it decomposes explosively at pressures as low as 1 mBar and may sensitise flammable gas mixtures even as a minor impurity [10]. It is usually prepared [4] in solution in a solvent, and such solutions in chloroform are reported as stable up to 18% concentration. However, an 18% solution in dibutyl ether exploded on cooling in a refrigerator, and a 12% solution prepared without cooling had decomposed vigorously [5]. In absence of other materials, explosion of the trichloride may be initiated in a wide variety of ways. The solid frozen under vacuum in liquid nitrogen explodes on thawing, and the liquid explodes on heating to 60 or 95°C. Exposure to impact, light or ultrasonic irradiation will cause (or sensitise) detonation [1]. The preparation and synthetic use of solutions of nitrogen trichloride in dichloromethane is described in detail [6]. Trichloramine is surprisingly stable, can be formed at 80°C and above, and has been made in 200 kg lots for possible use as a chlorinating agent [7]. The formation and separation of the trichloride have been described in detail [8]. Most of the early 19th century experimenters with nitrogen trichloride were injured by explosions thereof [9].

See Chlorine: Nitrogen compounds, or: Dimethyl phosphoramidate
Phosphorus pentachloride: Urea
Sodium chloride: Nitrogen compounds

See other IRRADIATION DECOMPOSITION INCIDENTS

Chlorine, Hydrogen

Ashmore, P. G., *Nature*, 1953, **172**, 449—450

Equimolar mixtures of chlorine and hydrogen containing 0.1—0.2% of the trichloride will explode in absence of light if the pressure is below a limiting value dependent on temperature (30 mbar at 20°, 132 mbar at 57°C).

Initiators

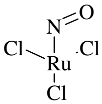
1. Mellor, 1940, Vol. 8, 601—604; 1967, Vol. 8, Suppl. 2.2, 412
2. Pascal, 1956, Vol. 10, 264

A wide variety of solids, liquids and gases will initiate the violent and often explosive decomposition of nitrogen trichloride. These include conc. ammonia, arsenic, dinitrogen tetraoxide (above —40°C, with more than 25% solutions of trichloride in chloroform), hydrogen sulfide, hydrogen trisulfide, nitrogen oxide, organic matter (including grease from the fingers), ozone, phosphine, phosphorus (solid, or in carbon disulfide solution), potassium cyanide (solid, or aqueous solution), potassium hydroxide solution or selenium [1]. All four hydrohalide acids will also initiate explosion of the trichoride [2].

See other ENDOTHERMIC COMPOUNDS, N-HALOGEN COMPOUNDS

4138. Nitrosylruthenium trichloride

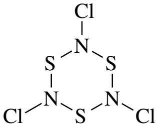
[18902-42-6] **Cl_3NORu**



Sidgwick, 1950, 1486

It decomposes violently at 440°C.
See other N-METAL DERIVATIVES, NITROSO COMPOUNDS

4139. 1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine (Thiazyl chloride)
[18428-81-4] **$Cl_3N_3S_3$**

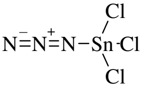


Bailar, 1973, Vol. 2, 908
It explodes violently on sudden heating.

Ammonia, Silver nitrate
Goehring, 1957, 67
Thiazyl chloride, treated with aqueous ammonia and then silver nitrate, gives a compound AgN_5S_3 (of unknown structure) which is shock-sensitive and explodes violently.

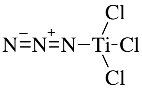
Hexacarbonylmolybdenum
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum
See Carbonyl(pentasulfur pentanitrido)molybdenum
See other N-HALOGEN COMPOUNDS, N—S COMPOUNDS

4140. Tin azide trichloride
[ ] **Cl_3N_3Sn**



An explosive solid.
See entry METAL AZIDE HALIDES

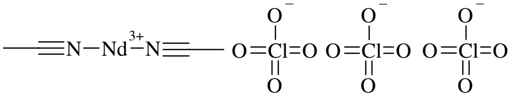
4141. Titanium azide trichloride
[ ] **Cl_3N_3Ti**



An explosive solid.
See entry METAL AZIDE HALIDES

4142. Neodymium perchlorate . 2acetonitrile

[13498-06-1] **$Cl_3NdO_{12}.2C_2H_3N$**



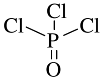
1. Forsberg, J. H. *et al., Inorg. Chem.*, 1971, **10**, 2656
2. Eigenbrot, C. W. *et al., Inorg. Chem.*, 1982, **21**, 2867
3. Raymond, K. N., *Chem. Eng. News*, 1983, **61**(49), 4
4. Bretherick, L., *Chem. Eng. News*, 1983, **61**(50), 2

The perchlorate, prepared from neodymium oxide and perchloric acid [1] was purified and isolated as the salt tetrasolvated with acetonitrile [2], which has not been found to be shock-sensitive. On vacuum drying at 80°C/24h, it is converted to the disolvated salt which is very shock-sensitive and a 1 g sample exploded violently in a hand-held flask [3]. Other examples of partially desolvated perchlorate salts becoming friction- and shock-sensitive are known [4]. (The disolvate is very close to zero oxygen balance).

See other METAL PERCHLORATES, SOLVATED OXOSALT INCIDENTS

4143. Phosphoryl chloride

[10025-87-3] **Cl_3OP**



(*MCA SD-26*, 1968); *HCS 1980*, 751

Acetone

1. Anon., *Sichere Chemiearbeit*, 2005, **57**(2),
2. Brenek, S. J. *et al., Org. Process Res. & Dev.*, 2000, **4**(6), 585

A drum of phosphoryl chloride, recovered by distillation, burst some ten hours after filling. The line and pump used for transfer had been cleaned with acetone, pockets of which probably remained. Calorimetry revealed that, starting at 30°C, unmixed and unstirred acetone and oxychloride (molar ratio not reported) heated slowly to 55°C over two hours and thereafter ran-away to 180° and substantial pressure in a few minutes. It was concluded that acetone was the cause of the mishap, and probably of some other incompletely explained prior accidents (see below) [1]. An earlier accident on laboratory scale had also been both reported and thermally investigated [2].

See Acetone

Carbon disulfide MRH Carbon disulfide 1.17/99+

Disposal of a benzene solution of phosphoryl chloride into a waste drum containing carbon disulfide (and other solvents) caused an instantaneous reaction, with evolution of (probably) hydrogen chloride. Presence of a hydroxylic compound seems likely.

Dimethyl sulfoxide MRH 1.80/99+

See Dimethyl sulfoxide: Acyl halides

Dimethylaniline

Anon., private comm., 1984

In a chlorination reaction using phosphoryl chloride with dimethylaniline as acid acceptor, the reagents were added all at once. After an induction period, most of the mixture was ejected from the flask. On a smaller scale, the reaction had been uneventful.

Dimethylformamide, 2,5-Dimethylpyrrole

MCA Case History No. 1460

Poor stirring during formylation of 2,5-dimethylpyrrole with the preformed complex of dimethylformamide with phosphoryl chloride caused eruption of the flask contents. Reaction of the complex with a local excess of the pyrrole may have been involved.

2,6-Dimethylpyridine *N*-oxide

1. Kato, T. *et al., J. Pharm. Soc. Japan.*, 1951, **71**, 217
2. Anon., *Chem. Eng. News*, 1965, **43**(47), 40
3. Evans, R. F. *et al., J. Org. Chem.*, 1962, **27**, 1333

Interaction of the reagents in absence of diluent, according to a published procedure [1], caused an explosion [2]. The use of a chlorinated solvent as diluent prevented explosion, confirming an earlier report [3].

See Pyridine *N*-oxide, below

Ferrocene-1,1'-dicarboxylic acid

Marvel, C. S., *Chem. Eng. News*, 1962, **40**(3), 55

An explosion occurred immediately after pouring and capping of the chloride recovered from preparation of ferrocene-1,1'-dicarbonyl chloride. The storage bottle contained phosphoryl chloride recovered from similar preparations and which had been stored for some 3 months. No explanation was apparent.

Other reactants

Yoshida, 1980, 76

MRH values calculated for 10 combinations with various reagents are given.

Pyridine *N*-oxide

MCA Guide 1972, 321

Dropwise addition of the chloride caused a steady exotherm to 60—65°C when a runaway reaction accelerated to explosion.

See 2,6-Dimethylpyridine *N*-oxide, above

Sodium MRH 4.27/31

See Sodium: Non-metal halides (reference 7)

Water

1. *MCA SD-26*, 1968
2. Unpublished observations
3. *MCA Case History No. 1274*
4. *MCA Case History No. 2286*

5. Anon., *Loss Prev. Bull.*, 1972, (013), 22—23
6. Anon., *Loss Prev. Bull.*, 1980, (038), 27
7. Anon., *Sichere Chemiearb.*, 1985, **37**(11), 130
8. Davies, R., *Loss Prev Bull.*, 1995, 121, 13

The hazards arising from interaction of phosphoryl chloride and water derive from there being often a considerable delay in onset of the exothermic hydrolysis reaction, which may proceed with enough vigour to generate steam and liberate hydrogen chloride gas. Conditions tending to favour delayed or violent reaction include limited quantities of water and/or ice for hydrolysis, lack of stirring, cold or frozen phosphoryl chloride, and reaction in closed or virtually closed containers [1]. A layer of the dense and cold liquid may survive for several minutes under water before violent, almost instantaneous hydrolysis occurs, particularly when disturbed [2]. The Case History describes a violent explosion which occurred when water was added to a drum containing some phosphoryl chloride which had been stored below its freezing point, 2°C [3]. Bursting of a 300 kg drum during filling was attributed to delayed reaction of the chloride with water contamination in the drum [4]. Methods for the safe decontamination of non-returnable drums which have contained the chloride are detailed, and involve thorough draining of the drum and internal inspection before careful application of large amounts of water [5]. When 10 l of the chloride was sucked into a measuring vessel, a violent explosion occurred which ruptured it. It was assumed that water previously used to clean the vessel had not fully drained out [6]. In outdoor storage, rainwater found its way into the space between the outer container and the polythene liner containing solid methylchlorouracil. When this was tipped into phosphoryl chloride in a reactor, some 4—5 l of water also ran in and caused an explosive evolution of hydrogen chloride gas which led to a fatality [7]. An account of an explosion when a transfer hose largely full of phosphoryl chloride was flushed with water is given [8].

See other GAS EVOLUTION INCIDENTS, PLANT CLEANING INCIDENTS

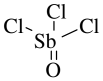
Zinc MRH 1.34/39

Mellor, 1940, Vol. 8, 1025

Zinc dust ignites in contact with a little phosphoryl chloride, and subsequent addition of water liberates phosphine which ignites.

See other NON-METAL HALIDES (AND THEIR OXIDES)

4144. Antimony trichloride oxide (Antimonyl chloride)
[14459-54-2] **Cl_3OSb**



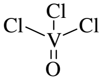
Bromine trifluoride

See Bromine trifluoride: Antimony trichloride oxide

See related METAL HALIDES, METAL OXIDES

4145. Vanadium trichloride oxide (Vanadyl chloride)

[7727-18-6] **Cl_3OV**



HCS 1980, 953

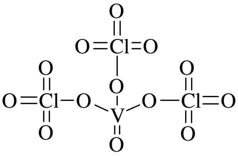
Bailar, 1973, Vol. 3, 508
The chloride (and analogous bromide) is violently hygroscopic.

Rubidium
See Rubidium: Vanadium trichloride oxide

Sodium
Quam, G. N. *et al.*, in *Safety in the Chemical Laboratory*, (Ed. Steere, N.V.), Vol. 1, 1967, 82 (expanded articles reprinted from *J. Chem. Educ.*, 1964—67)
In a procedure to purify the chloride oxide with sodium, too-rapid addition of the metal led to a violent explosion.
See Sodium: Metal halides (reference 2)
See related METAL HALIDES, METAL OXIDES

4146. Vanadyl perchlorate

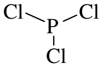
[63672-69-3] **$Cl_3O_{13}V$**



Alone, or Organic solvents
Schmeisser, M., *Angew. Chem.*, 1955, **67**, 499
A powerful oxidant which may explode above 80°C, and which ignites organic solvents on contact. It decomposes, sometimes explosively, on exposure to light.
See other METAL PERCHLORATES, OXIDANTS

4147. Phosphorus trichloride

[7719-12-2] **Cl_3P**



(*MCA SD-27*, 1972); *HCS 1980*, 749

Carboxylic acids
1. Coghill, R. D., *J. Amer. Chem. Soc.*, 1938, **60**, 488
2. Peacocke, T. A., *School Sci. Rev.*, 1962, **44**(152), 217

3. Scrimgeour, C. M., *Chem. Brit.*, 1975, **11**, 267
4. Taylor, D. A. H. *et al., Chem. Brit.*, 1976, **12**, 105
5. Bretherick, L., *Chem. Brit.*, 1976, **12**, 26

Use of a free flame instead of a heating bath to distil acetyl chloride produced from acetic acid and phosphorus trichloride caused the residual phosphonic ('phosphorous') acid to decompose violently to give spontaneously flammable phosphine [1]. Two later explosions in the same preparative system after reflux but before distillation from a water-bath may have been due to ingress of air into the cooling flask and ignition of traces of phosphine [2]. During preparation of furoyl chloride, the excess trichloride was distilled off at atmospheric pressure, then vacuum was applied prior to intended distillation at 100°C/100 mbar, and an explosion occurred shortly after [3]. A similar incident occurred during conversion of propionic acid to the chloride [4]. These incidents were attributed to thermal decomposition of the by-product phosphonic acid to give a phosphine—diphosphane mixture and leakage of air into the evacuated system to produce a spontaneously explosive mixture. Sulfinyl chloride is a safer chlorinating agent for carboxylic acids [5].

Chlorobenzene, Sodium
See Sodium: Chlorobenzene, etc.

Dimethyl sulfoxide
See Dimethyl sulfoxide: Acyl halides, etc.

Hexafluoroisopropylideneaminolithium
See Hexafluoroisopropylideneaminolithium: Non-metal halides

Hydroxylamine
See Hydroxylamine: Phosphorus chlorides

Metals MRH Potassium 2.80/46, sodium 3.10/33
Mellor, 1940, Vol. 8, 1006; 1941, Vol. 2, 470
Potassium ignites in phosphorus trichloride, while molten sodium explodes on contact.
See Aluminium: Non-metal halides

Nitroheterocycle
Hallam. S., 1993, personal communication
A multi-kg mixture of the trichloride and a nitroheterocycle obtained after de-oxygenation of the corresponding N-oxide was being worked up by distillation under vacuum. It burst the glass vessel. Investigation showed that this was due to a higher temperature (85—90°C) than previously employed, permitting the phosphorus trichloride to react vigorously with the product.

Other reactants
Yoshida, 1980, 59
MRH values calculated for 8 combinations with various reagents are given.

Oxidants MRH values show % of oxidant
See Chromium pentafluoride: Phosphorus trichloride
Chromyl chloride: Non-metal halides

Fluorine: Phosphorus halides
Iodine chloride: Phosphorus trichloride
Lead(IV) oxide: Non-metal halides MRH 0.67/69
Nitric acid: Phosphorus halides MRH 0.63/31
Selenium dioxide: Phosphorus trichloride
Sodium peroxide: Non-metal halides MRH 2.55/46

Oxygen

Vorob'ev, N. I. *et al., Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1974, **10**, 2039—2042

Interaction to form phosphoryl chloride at 100—700°C was investigated, and the limiting concentrations to prevent explosions were determined.

Sodium Carbonate

Holmes, W. S., 1989, personal communication

This is often recommended for clearing up spillage. A dangerously vigorous reaction can result (probably depending upon the hydration level of the carbonate?). Large quantities of dry sand followed by addition to water are preferred.

See Water, below

Sulfur acids

Dillon, K. B. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 883—885

The trichloride is initially insoluble in 100% sulfuric acid, fluorosulfuric acid or 25% oleum, but dissolves very exothermally after delays of 8, 1 and 0.5 h, respectively. Reaction with 65% oleum is immediately violent.

See Phosphorus tribromide: Sulfur acids
See Phosphorus triiodide: Sulfur acids
See other INDUCTION PERIOD INCIDENTS

Tetravinyllead

See Tetravinyllead: Phosphorus trichloride

Water

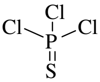
1. *MCA SD-27*, 1972
2. Albright and Wilson, (Manufacturer's safety sheet)
3. Coghill, R. D., *J. Amer. Chem. Soc.*, 1938, **60**, 488
4. *MCA Case History No. 520*
5. Anon., *Loss. Prev. Bull.*, 1977, (013), 21—23
6. Melhem, G. A. *et. al., Process Safety Progr.,*, 1998, **17**(1), 49

Reaction with water is exothermic and immediately violent (unlike phosphoryl chloride), and is accompanied by evolution of some diphosphane which ignites [1]. There can sometimes be an induction period, especially if cold. Yellow solids produced by hydrolysis may ignite spontaneously if dried [2]. Evaporation of the trichloride from an open beaker on a steam-bath led to ignition, which did not occur if a hotplate were used as a dry heat source [3]. Interaction of the trichloride and water in a virtually sealed container caused the latter to burst under the pressure of hydrogen chloride generated [4]: (1 vol. trichloride gives 830 vol. of hydrogen chloride at 20°C). A detailed but not especially enlightening study of the reaction of water and phosphorus trichloride leading to mixing of the initially separate layers and runaway.

The authors detected no phosphine [6]. Methods for the safe decontamination of non-returnable drums which have contained the chloride are detailed, and involve careful application of large amounts of water to the well-drained drum [5].
See other GAS EVOLUTION INCIDENTS, NON-METAL HALIDES (AND THEIR OXIDES)

4148. Thiophosphoryl chloride

[3982-91-0] **Cl_3PS**



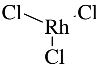
Möller, T. *et al., Inorg. Synth.*, 1954, **4**, 72
During the preparation from phosphorus trichloride and sulfur, the quantity and quality of the aluminium chloride catalyst is critical to prevent the exothermic reaction going out of control.

Methylmagnesium iodide
See Tetramethyldiphosphane disulfide

Pentaerythritol
MCA Case History No. 1315
On two occasions violent explosions occurred after heating of equimolar proportions of the reagents (for 4 h at 160°C according to a literature method) had been discontinued. (This suggests spontaneous ignition of traces of phosphine derivatives as air was drawn into the cooling reaction vessel).
See Phosphorus trichloride: Carboxylic acids (reference 5)
See related NON-METAL HALIDES

4149. Rhodium(III) chloride

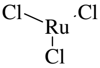
[10049-07-7] **Cl_3Rh**



Pentacarbonyliron, Zinc
See Pentacarbonyliron: Transition metal halides
See other METAL HALIDES

4150. Ruthenium(III) chloride

[10049-08-8] **Cl_3Ru**



Hydrazine
See Hydrazine: Ruthenium(III) chloride

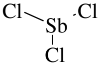
Pentacarbonyliron, Zinc

See Pentacarbonyliron: Transition metal halides

See other METAL HALIDES

4151. Antimony trichloride

[10025-91-9] **Cl_3Sb**



(*MCA SD-66*, 1957); *HCS 1980*, 164

Aluminium

See Aluminium: Antimony trichloride

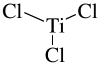
N-Chlorodimethylamine

See N-chlorodimethylamine: Antimony chlorides

See other METAL HALIDES

4152. Titanium trichloride

[7705-07-9] **Cl_3Ti**



HCS 1980, 905

Air, or Water

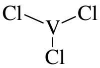
1. Lerner, R. W., *Ind. Eng. Chem.*, 1961, **53**(12). 56A
2. Ingraham, T. K. *et al., Inorg. Synth.*, 1960, **5**, 56

It reacts vigorously with air and/or water (vapour or liquid) and adequate handling precautions are necessary [1]. The finely divided powder is pyrophoric in air [2].

See other METAL HALIDES, PYROPHORIC MATERIALS, REDUCANTS

4153. Vanadium trichloride

[7718-98-1] **Cl_3V**



Methylmagnesium iodide

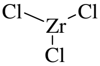
Cotton, F. A., *Chem. Rev.*, 1955, **55**, 560

Reaction of vanadium trichloride and similar halides with Grignard reagents is almost explosively violent under a variety of conditions.

See other METAL HALIDES, REDUCANTS

4154. Zirconium trichloride

[10241-03-9] **Cl_3Zr**



Water

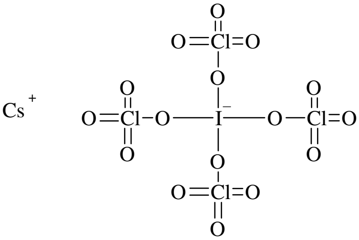
Pascal, 1963, Vol. 9, 540

Interaction is very violent, hydrogen being evolved.

See other METAL HALIDES, REDUCANTS

4155. Caesium tetraperchloratoiodate

[53078-10-7] **Cl_4CsIO_{16}**



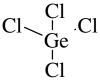
Christe, K. O. *et al., Inorg. Chem.*, 1972, **11**, 683

Though stable at ambient temperature, samples exploded under laser irradiation at low temperatures.

See other IODINE COMPOUNDS, IRRADIATION DECOMPOSITION INCIDENTS, NON-METAL PERCHLORATES

4156. Germanium tetrachloride

[10038-98-9] **Cl_4Ge**



Water

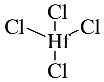
Mellor, 1941, Vol. 7, 270

Interaction is very exothermic, accompanied by crackling if the chloride is dropped into water.

See other METAL HALIDES

4157. Hafnium tetrachloride

[13499-05-3] **Cl_4Hf**



Tetrahydrofuran

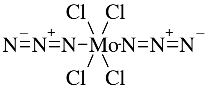
Manzer, L. E., *Inorg. Synth.*, 1982, **21**, 137

Addition of the anhydrous chloride directly to THF causes a violent exothermic reaction. Add THF dropwise to a suspension of the chloride in dichloromethane.

See other METAL HALIDES

4158. Molybdenum diazide tetrachloride

[14259-66-6] **Cl_4MoN_6**

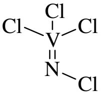


Highly explosive.

See entry METAL AZIDE HALIDES

4159. Chloriminovanadium trichloride

[14989-38-9] **Cl_4NV**



1. Strähle, J. *et al., Angew. Chem.*, 1966, **78**, 450
2. Strähle, J. *et al., Z. Anorg. Chem.*, 1965, **338**, 287

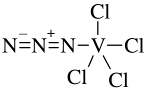
A new method of preparation from vanadium nitride and chlorine [1] is free of the explosion hazards of chlorine azide and vanadium azide tetrachloride present in an earlier method [2].

See other AMMINEMETAL HALIDES, N-HALOGEN COMPOUNDS

See related METAL HALIDES

4160. Vanadium azide tetrachloride

[ ] **Cl_4N_3V**

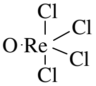


Explosive solid.

See entry METAL AZIDE HALIDES

4161. Rhenium tetrachloride oxide

[13814-76-1] **Cl_4ORe**



Ammonia

Sidgwick, 1950, 1302

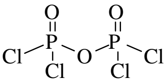
Interaction with gaseous or liquid ammonia is violent.

See other AMINATION INCIDENTS

See related METAL HALIDES, METAL OXIDES

4162. Diphosphoryl chloride

[13498-14-1] **$Cl_4O_3P_2$**



Water

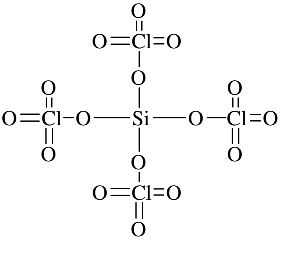
Mellor, 1971, Vol. 8, Suppl. 3, 505

Hydrolysis is as vigorous as that of phosphorus pentoxide.

See other NON-METAL HALIDES

4163. Tetraperchloratosilicon

[ ] **$Cl_4O_{16}Si$**



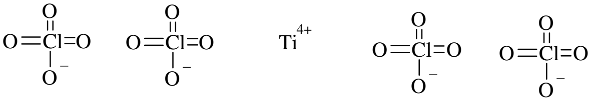
1. Sorbe, 1968, 127
2. Schmeisser, M., *Angew. Chem.*, 1955, **67**, 499

A highly explosive liquid [1]. Early attempts failed to isolate it but prepared numerous other explosive compounds. Reaction of dichlorine hexoxide with silicon tetrachloride or tetrabromide gave an explosive solid, apparently a perchlorato oligosiloxane. Silver perchlorate and silicon tetrahalides in ether gave explosive volatile organics, perhaps ethyl perchlorate. Replacing ether by acetonitrile as solvent, a solid (di)acetonitrile adduct of the tetraperchlorate precipitated, described as exceptionally explosive even in the smallest quantities [2].

See other NON-METAL PERCHLORATES

4164. Titanium tetraperchlorate

[60580-20-3] **$Cl_4O_{16}Ti$**



Kirk Othmer, 4th. Edn., 1996, Vol. 18, 161

The compound sublimes from 70°C and explodes on heating to 130°C at atmospheric pressure.

Diethyl ether, or Formamide, or Dimethylformamide

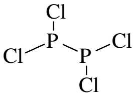
Laran, R. J., US Pat. 3 157 464, 1964

Described as insensitive to heat or shock, this powerful oxidant explodes on contact with diethyl ether, and ignites with formamide or DMF.

See other METAL PERCHLORATES, OXIDANTS

4165. Tetrachlorodiphosphane

[13497-91-1] **Cl_4P_2**



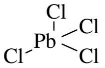
Besson, A. *et al., Compt. rend.*, 1910, **150**, 102

It oxidises rapidly in air, sometimes igniting.

See other HALOPHOSPHINES, NON-METAL HALIDES

4166. Lead tetrachloride

[13463-30-4] **Cl_4Pb**



1. Bailar, 1973, Vol. 2, 136, 1066
2. Kaufmann, G. B. *et al., Inorg. Synth.*, 1983, **22**, 150

It may disproportionate explosively to lead(II) chloride and chlorine above 100°C [1]. Preparative precautions are detailed [2].

Potassium

See Potassium: Metal halides

Sulfuric acid

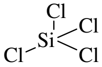
Friedrich, H., *Ber.*, 1893, **26**, 1434

It explodes on warming with diluted sulfuric acid or on attempted distillation from the concentrated acid in a stream of chlorine.

See other METAL HALIDES

4167. Tetrachlorosilane (Silicon tetrachloride)

[10026-04-7] **Cl_4Si**



HCS 1980, 821

Dimethyl sulfoxide

See Dimethyl sulfoxide: Acyl halides, etc.

Ethanol, Water

Skinner, S. J., *Loss. Prev.*, 1981, **14**, 178—180

In the preparation of ethyl polysilicate by mixing tetrachlorosilane and industrial methylated spirit containing some water, failure of the agitator is thought to have led to layering of the alcohol over the dense chloride. Evolution of hydrogen chloride led to mixing of the layers, and a greatly increased rate of reaction and self-accelerating gas evolution which burst the reactor.

See other AGITATION INCIDENTS, GAS EVOLUTION INCIDENTS

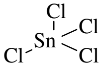
Sodium

See Sodium: Non-metal halides (reference 8)

See other HALOSILANES, NON-METAL HALIDES

4168. Tin(IV) chloride

[7646-78-8] **Cl_4Sn**



HCS 1980, 902

Alkyl nitrates

See ALKYL NITRATES: Lewis acids

Ethylene oxide

See Ethylene oxide: Contaminants

Nitrobenzene

See Nitrobenzene: Tin(IV) chloride

Turpentine

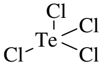
Mellor, 1941, Vol. 7, 446

Interaction is strongly exothermic and may lead to ignition.

See other METAL HALIDES

4169. Tellurium tetrachloride

[10026-07-0] **Cl_4Te**



Ammonia

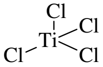
Mellor, 1943, Vol. 11, 58

Interaction with liquid ammonia at —15°C forms tellurium nitride (?), which explodes at 200°C.

See other NON-METAL HALIDES

4170. Titanium tetrachloride

[7550-45-0] **Cl_4Ti**



HCS 1980, 904

Lithium nitride

See Lithium nitride: Transition metal halides

Sulfur nitrides

See Disulfur dinitride: Metal chlorides

Tetrasulfur tetranitride: Metal chlorides

Tetrahydrofuran

Manzer, L. E., *Inorg. Synth.*, 1982, **21**, 135

Addition of the anhydrous chloride directly to THF causes a violent exothermic reaction. Add THF dropwise to a suspension of the chloride in dichloromethane.

Urea

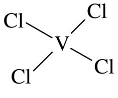
Ionova, E. A. *et al., Chem. Abs.*, 1966, **64**, 9219b

The liquid hexaurea complex formed during 6 weeks at 80°C decomposed violently at above 90°C. *N*-Halogen compounds may have been formed.

See other METAL HALIDES

4171. Vanadium tetrachloride

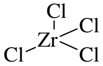
[7632-51-1] **Cl_4V**



Lithium nitride

See Lithium nitride: Transition metal halides

4172. Zirconium tetrachloride
[10026-11-6] **Cl_4Zr**



Ethanol, or Water

Rosenheim, A. *et al., Ber.*, 1907, **40**, 811

Interaction with either is violent.

Lithium, Nitrogen

See Lithium: Metal chlorides, etc.

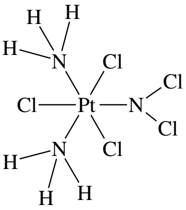
Tetrahydrofuran

Manzer, L. E., *Inorg. Synth.*, 1982, **21**, 136

Addition of the anhydrous chloride directly to THF causes a violent exothermic reaction. Add THF dropwise to a suspension of the chloride in dichloromethane.

See other METAL HALIDES

4173. Diamminedichloroamidotrichloroplatinum(IV)
[18815-16-2] **$Cl_5H_6N_3Pt$**

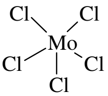


Kukushkin, Yu. N., *Chem. Abs.*, 1958, **52**, 13509i

It tended to decompose violently.

See other N-HALOGEN COMPOUNDS, PLATINUM COMPOUNDS

4174. Molybdenum pentachloride
[10241-05-1] **Cl_5Mo**



Sodium, or Sodium sulfide

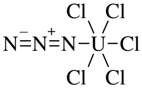
1. Berry, D. H., *Chem. Eng. News*, 1989, **67**(47), 2
2. Kaner, R. B., *Nature*, 1991, **349**, 510

Placing the chloride in contact with finely divided sodium caused an explosion after a short induction period [1]. Reaction with sodium sulfide gives molybdenum disulfide in a vigorous deflagration; autoignition will occur on mixing if the sodium sulfide is

finely divided. Using sintered sulfide, which is recommended, initiation may take place on local heating to less than 60°C [2].
See Sodium: Metal halides
See other METAL HALIDES

4175. Uranium azide pentachloride

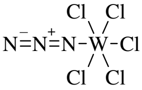
[55042-15-4] **Cl_5N_3U**



Explosive solid.
See entry METAL AZIDE HALIDES

4176. Tungsten azide pentachloride

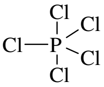
[88495-99-2] **Cl_5N_3W**



Extremely explosive.
See entry METAL AZIDE HALIDES

4177. Phosphorus pentachloride

[10026-13-8] **Cl_5P**



HCS 1980, 746

Aluminium MRH 2.76/17
See Aluminium: Non-metal halides

Carbamates
See *N*-Carbomethoxyiminophosphoryl chloride

Chlorine dioxide, Chlorine MRH Chlorine dioxide 1.55/29
Mellor, 1941, Vol. 2, 281; 1940, Vol. 8, 1013
Contact between phosphorus pentachloride and a mixture of chlorine and chlorine dioxide (previously considered to be dichlorine trioxide) usually causes explosion, possibly owing to formation of the more sensitive chlorine monoxide.

Fluorine
See Fluorine: Phosphorus halides

Hydroxylamine

See Hydroxylamine: Phosphorus chlorides

Magnesium oxide

Mellor, 1940, Vol. 8, 1016

A heated mixture incandesces brilliantly.

3'-Methyl-2-nitrobenzanilide

Partridge, M. W., private comm., 1968

The residue from interaction of the chloride and anilide in benzene after removal of solvent and phosphoryl chloride under vacuum exploded violently on admission of air.

Nitrobenzene MRH 4.52/99+

Unpublished observations

A solution of phosphorus pentachloride in nitrobenzene is stable at 110° but begins to decompose with accelerating violence above 120°C, with evolution of nitrous fumes.

Other reactants

Yoshida, 1980, 60

MRH values calculated for 8 combinations with varioue reagents are given.

Phosphorus(III) oxide

Mellor, 1940, Vol. 8, 898

Interaction is rather violent at ambient temperature.

Sodium MRH 4.89/35

See Sodium: Non-metal halides

Urea

Anon., *Angew. Chem. (Nachr.)*, 1960, **8**, 33

A dry mixture exploded after heating, probably owing to formation of nitrogen trichloride. Other chlorinating agents will react similarly with nitrogenous materials.

See Chlorine: Nitrogen compounds

Water

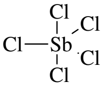
Mellor, 1940 Vol. 8, 1012

Interaction with water in limited quantities is violent, and the hydrolysis products may themselves react violently with more water.

See Phosphoryl chloride: Water

See other NON-METAL HALIDES

4178. Antimony pentachloride
[7647-18-9] **Cl_5Sb**



HCS 1980, 160

N-Chlorodimethylamine

See N-Chlorodimethylamine: Antimony chlorides

Oxygen difluoride

See Oxygen difluoride: Halogens, etc.

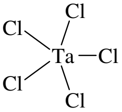
Phosphonium iodide

See Phosphonium iodide: Oxidants

See other METAL HALIDES, OXIDANTS

4179. Tantalum pentachloride

[7721-01-9] **Cl_5Ta**



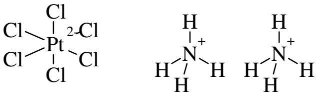
Lithium dimethylamide

See Pentakis(dimethylamino)tantalum(V)

See other METAL HALIDES

4180. Ammonium hexachloroplatinate

[1332-76-9] **$Cl_6H_8N_2Pt$**



Potassium hydroxide, Combustible materials

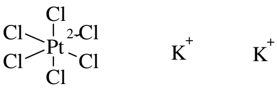
Mellor, 1942, Vol. 16, 336

Boiling ammonium hexachloroplatinate with alkali gives a product (possibly potassium hexahydroxyplatinate) which after drying will explode violently on heating alone or with combustible materials.

See other PLATINUM COMPOUNDS

4181. Potassium hexachloroplatinate

[1307-80-8] **Cl_6K_2Pt**



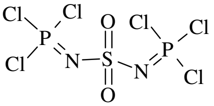
Bromine trifluoride

See Bromine trifluoride: Potassium hexachloroplatinate

See other PLATINUM COMPOUNDS

4182. Bis(trichlorophosphoranylidene)sulfamide

[14259-65-5] **$Cl_6N_2O_2P_2S$**



Cellulose, or Ethanol, or Water

Vandi, A. *et al., Inorg. Synth.*, 1966, **8**, 119

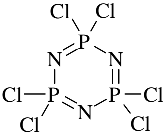
It is extremely reactive with water or alcohol, and causes filter paper to ignite.

See other N—S COMPOUNDS

See related NON-METAL HALIDES (AND THEIR OXIDES)

4183. Hexachlorocyclotriphosphazine

[940-71-6] **$Cl_6N_3P_3$**



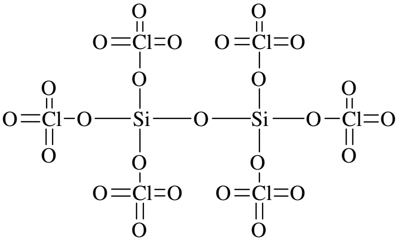
Dimethyl sulfoxide

See Dimethyl sulfoxide: Hexachlorocyclotriphosphazine

See related NON-METAL HALIDES

4184. Bis(triperchloratosilicon) oxide

[ ] **$Cl_6O_{25}Si_2$**



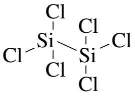
Schmeisser, M., *Angew. Chem.*, 1955, **67**, 499

This solid decomposition product of tetraperchloratosilicon was so explosive, even in small amounts, that work was discontinued.

See related NON-METAL PERCHLORATES

4185. Hexachlorodisilane

[13465-77-5] **Cl_6Si_3**



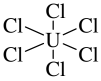
See entry HALOSILANES

Chlorine

See Chlorine: Hexachlorodisilane

4186. Uranium hexachloride

[13763-23-0] **Cl_6U**



Water

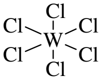
Bailar, 1973, Vol. 5, 189

Interaction is violent.

See other METAL HALIDES

4187. Tungsten hexachloride

[13283-01-7] **Cl_6W**



Sodium sulfide

Kaner, R. B., *Nature*, 1991, **349**, 510

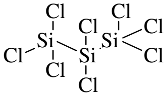
Reacts with sodium sulfide even more exothermically than molybdenum pentachloride.

See Molybdenum pentachloride.

See other METAL HALIDES

4188. Octachlorotrisilane

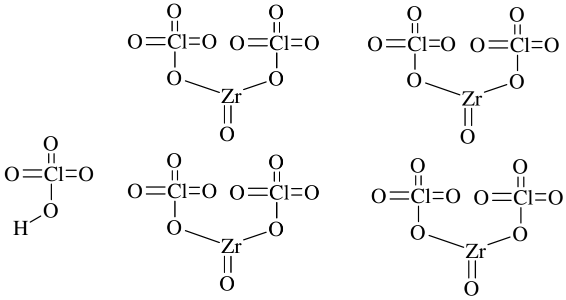
[13596-23-1] **Cl_8Si_3**



See entry HALOSILANES

4189. Tetrazirconium tetraoxide hydrogen nonaperchlorate

[ ] **$Cl_9HO_{40}Zr_4$**



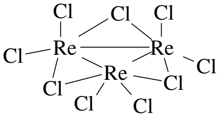
Mellor, 1946, Vol. 2, 403

The salt, 'zirconyl perchlorate', explodes if heated rapidly. Later work suggests alternative formulations for the salt.

See other METAL PERCHLORATES

4190. Trirhenium nonachloride

[14973-59-2] **Cl_9Re_3**



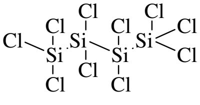
Oxygen

See Oxygen: Trirhenium nonachloride

See other METAL HALIDES

4191. Decachlorotetrasilane

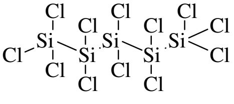
[13763-19-4] **$Cl_{10}Si_4$**



See entry HALOSILANES

4192. Dodecachloropentasilane

[13596-24-2] **$Cl_{12}Si_5$**



See entry HALOSILANES

4193. Cobalt

[7440-48-4] **Co**

Co

1. Bailar, 1973, Vol. 3, 1056
2. Chadwell, A. J. *et al., J. Phys. Chem.*, 1956, **60**, 1340

Finely divided cobalt is pyrophoric in air [1]. Raney cobalt catalyst appears to be less hazardous than Raney nickel [2].

Acetylene MRH 8.70/99+

See Acetylene: Cobalt

Hydrazinium nitrate

See Hydrazinium nitrate: Alome, or Metals, etc.

Other reactants

Yoshida, 1980, 120

MRH values calculated for 11 combinations, largely with oxidants, are given.

Oxidants MRH value shows % of oxidant

See Ammonium nitrate: Metals MRH 2.55/58

Bromine pentafluoride: Acids, etc.

Nitryl fluoride: Metals

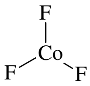
1,3,4,7-Tetramethylisoindole

See 1,3,4,7-Tetramethylisoindole: Cobalt

See other METALS, PYROPHORIC METALS

4194. Cobalt trifluoride

[10026-18-3] **CoF_3**



Hydrocarbons, or Water

Priest, H. F., *Inorg. Synth.*, 1950, **3**, 176

It reacts violently with hydrocarbons or water, and finds use as a powerful fluorinating agent.

Silicon

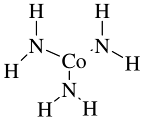
Mellor, 1956, Vol. 2, Suppl. 1, 64

A gently warmed mixture reacts exothermally, attaining red-heat.

See other METAL HALIDES

4195. Cobalt(III) amide

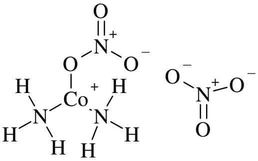
[ ] **CoH_6N_3**



Schmitz-Dumont, O. *et al., Z. Anorg. Chem.*, 1941, **284**, 175
Heating converts it to pyrophoric cobalt(III) nitride.
See other N-METAL DERIVATIVES

4196. Diamminenitratocobalt(II) nitrate

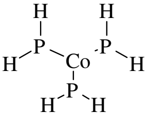
[33362-98-0] **$CoH_6N_4O_6$**



McPherson, G. L. *et al., Inorg,. Chem.*, 1971, **10**, 1574
A sample of the molten salt exploded at 200°C.
See other AMMINEMETAL OXOSALTS, REDOX COMPOUNDS

4197. Cobalt tris(dihydrogenphosphide)

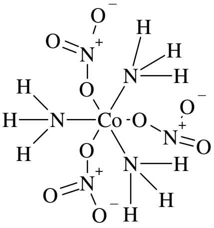
[ ] **CoH_6P_3**



Zehr, J., *Staub*, 1962, **22**, 494—508
It ignites in air, especially when finely divided.
See related NON-METAL HYDRIDES, PHOSPHINES

4198. Triamminetrinitrocobalt(III)

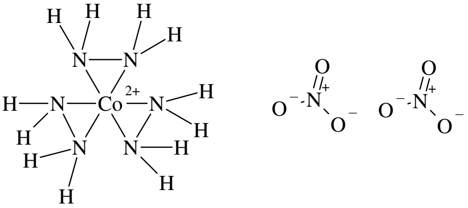
[13600-88-9] **$CoH_9N_6O_6$**



Explodes at 305°C, medium impact-sensitivity.
See entry AMMINEMETAL OXOSALTS (reference 2)

4199. Trihydrazinecobalt(II) nitrate

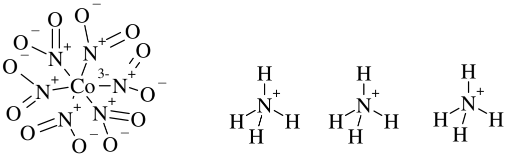
[82434-33-1] **$CoH_{12}N_8O_6$**



Franzen, H. *et al., Z. Anorg. Chem.*, 1908, **60**, 247, 274
It is explosive.
See other AMMINEMETAL NITRATES

4200. Ammonium hexanitrocobaltate(3—)

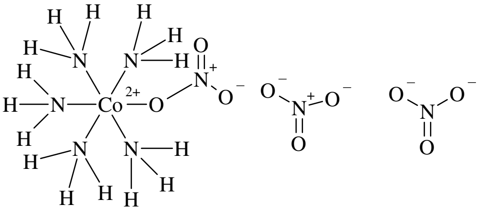
[14652-46-1] **$CoH_{12}N_9O_{12}$**



Explodes at 230°C, medium impact-sensitivity.
See entry AMMINEMETAL OXOSALTS (reference 2)

4201. Pentaamminenitratocobalt(III) nitrate

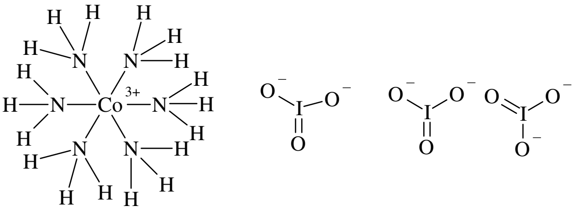
[14404-36-5] **$CoH_{15}N_8O_9$**



Explodes at 310°C, medium impact-sensitivity.
See entry AMMINEMETAL OXOSALTS (reference 2)

4202. Hexaamminecobalt(III) iodate

[14589-65-2] **$CoH_{18}I_3N_6O_9$**

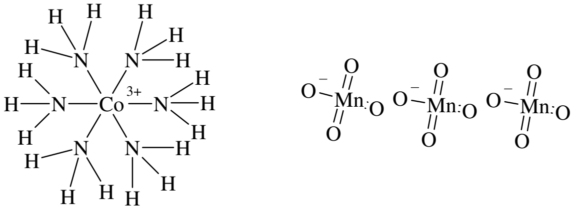


Explodes at 355°C, low impact-sensitivity.

See entry AMMINEMETAL OXOSALTS (reference 2)

4203. Hexaamminecobalt(III) permanganate

[22388-72-3] **$CoH_{18}Mn_3N_6O_{12}$**



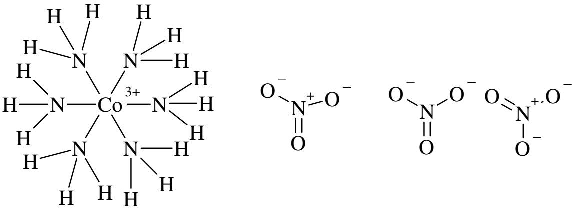
1. Mellor, 1942, Vol. 12, 336
2. Joyner, T. B., *Can. J. Chem.*, 1969, **47**, 2730

It explodes on heating [1], and is of treacherously high impact-sensitivity [2].

See other AMMINEMETAL OXOSALTS

4204. Hexaamminecobalt(III) nitrate

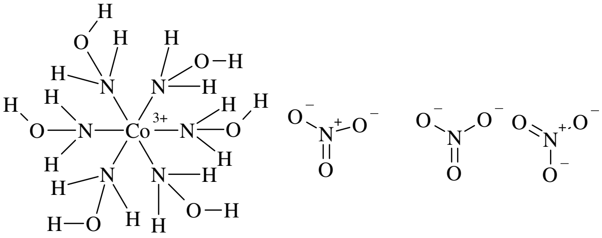
[10534-86-8] **$CoH_{18}N_9O_9$**



Explodes at 295°C, medium impact-sensitivity.

See entry AMMINEMETAL OXOSALTS (reference 2)

4205. Hexahydroxylaminecobalt(III) nitrate
[18501-44-5] (ion) **$CoH_{18}N_9O_{15}$**

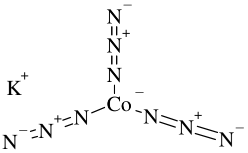


Werner, A. *et al., Ber.*, 1905, **38**, 897

It usually explodes during preparation or handling.

See other AMMINEMETAL OXOSALTS

4206. Potassium triazidocobaltate(1—)
[52324-65-9] **$CoKN_9$**



1. Fritzer, H. P. *et al., Angew. Chem. (Intern Ed.)*, 1971, **10**, 829
2. Fritzer, H. P. *et al., Inorg. Nucl. Chem. Lett.*, 1974, **10**, 247—252

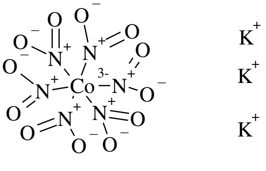
The complex azide is highly explosive and must be handled with extreme care. The analogous potassium and caesium derivatives of zinc azide and nickel azide deflagrate strongly in a flame and some are shock-sensitive [1]. The potassium salt alone out of 8 azido-complexes exploded during X-irradiation in an ESCA study [2].

See AZIDE COMPLEXES OF COBALT(III)

See other IRRADIATION DECOMPOSITION INCIDENTS

See related METAL AZIDES

4207. Potassium hexanitrocobaltate(3—)
[13782-01-9] **$CoK_3N_6O_{12}$**



1. Broughton, D. B. *et al., Anal. Chem.*, 1947, **19**, 72
2. Horowitz, O., *Anal. Chem.*, 1948, **20**, 89
3. Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 375

Evaporation by heating a filtrate from precipitation of 'potassium cobaltinitrite' caused it to turn purple and explode violently [1]. This was attributed to interaction of nitrite, nitrate, acetic acid and residual cobalt with formation of fulminic or methylnitrolic acids or their cobalt salts, all of which are explosive [2]. Mixtures containing nitrates, nitrites and organic materials are potentially dangerous, especially in presence of acidic materials and heavy metals. A later publication confirms the suggestion of formation of nitro- or nitrito-cobaltate(III) [3].
See related METAL NITRITES

4208. Cobalt(III) nitride

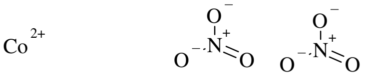
[12139-70-7] **CoN**

Co^{3+} N^{3-}

Schmitz-Dumont, O., *Angew. Chem.*, 1955, **67**, 231
A pyrophoric powder.
See Cobalt(III) amide
See other NITRIDES, PYROPHORIC MATERIALS

4209. Cobalt(II) nitrate

[10026-22-9] **CoN_2O_6**



HCS 1980, 321

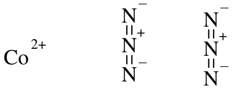
Ammonium hexacyanoferrate(II)
Wolski, W. *et al., Acta Chim.* (Budapest), 1972, **72**, 25—32
Interaction is explosive at 220°C.
See Copper(II) nitrate: Ammonium hexacyanoferrate(II), or: Potassium hexacyanoferrate(II)

Carbon MRH 3.68/14
Crowther, J. R., private comm., 1970
Charcoal impregnated with the nitrate exploded lightly during sieving. Possibly a dust or 'black powder' explosion.

Other reactants
Yoshida, 1980, 195
MRH values calculated for 16 combinations with oxidisable materials are given.
See other METAL NITRATES, OXIDANTS

4210. Cobalt(II) azide

[14215-31-7] **CoN_6**



Mellor, 1940, Vol. 8, 355
It explodes at 200°C.
See also AMMINEMETAL AZIDES
See other METAL AZIDES

4211. Cobalt(II) oxide

[1307-96-6] **CoO**

$Co{=}O$

Hydrogen peroxide
See Hydrogen peroxide: Metals, etc.
See other METAL OXIDES

4212. Cobalt(II) sulfide

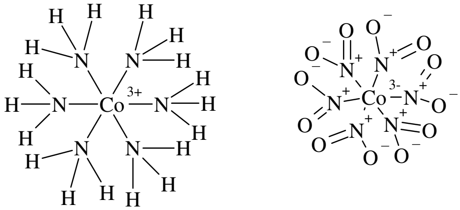
[1317-42-6] **CoS**

$Co{=}S$

Brauer, 1965, Vol. 2, 1523
Material dried at 300°C is pyrophoric.
See other METAL SULFIDES, PYROPHORIC MATERIALS

4213. Hexaamminecobalt(III) hexanitrocobaltate(3—)

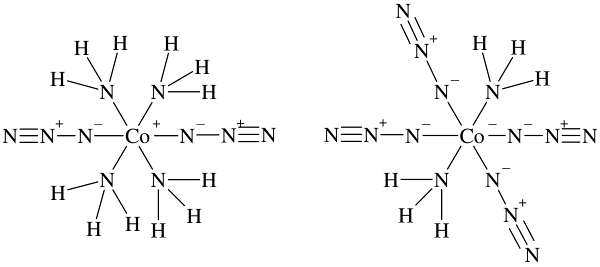
[15742-33-3] **$Co_2H_{18}N_{12}O_{12}$**



1. Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 376
2. Shidlovskii, A. A. *et al., Chem. Abs.*, 1977, **87**, 70416

An unstable compound of low impact-sensitivity [1]. In a comparative study of a series of cobalt complexes ranging from triamminecobalt(III) nitrite to ammonium hexanitrocobaltate(3—), the title compound burned the fastest [2].
See other AMMINEMETAL OXOSALTS

4214. *trans*-Tetraamminediazidocobalt(III) *trans*-diamminetetraazidocobaltate(1—)
[54689-17-7] **$Co_2H_{18}N_{24}$**



Druding, L. F. *et al., Inorg. Chem.*, 1975, **14**, 1365

During its preparation, solutions of the salt, which is a dangerous detonator, must not be evaporated to dryness. Surprisingly, mixtures with potassium bromide could be compressed (for IR examination) to 815 bar without decomposition. It contains 71% of nitrogen.

See AMMINEMETAL AZIDES, AZIDE COMPLEXES OF COBALT(III)

See other HIGH-NITROGEN COMPOUNDS

See related METAL AZIDES

4215. Cobalt(III) oxide
[1308-04-9] **Co_2O_3**

$Co^{3+}\quad Co^{3+}\quad O^{2-}\quad O^{2-}\quad O^{2-}$

(Commercial samples contain some cobalt(II) oxide)

Hydrogen peroxide

See Hydrogen peroxide: Metals, etc.

Nitroalkanes

See NITROALKANES: Metal oxides

See other METAL OXIDES

4216. Chromium
[7440-47-3] **Cr**

Cr

RSC Lab. Hazards Safety Data Sheet No. 65, 1987 (metal and compounds)

1. Sidgwick, 1950, 1013
2. Uel'skii, A. A. *et al., Chem. Abs.*, 1978, **89**, 116214

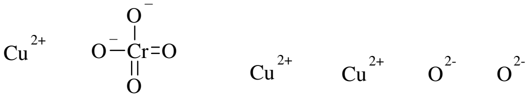
Evaporation of mercury from mercury amalgam leaves pyrophoric chromium [1]. Increasing the temperature at which hexacarbonylchromium is thermally decomposed increases the surface area and pyrophoricity of the chromium powder produced [2].

Carbon dioxide
See Carbon dioxide: Metals

Oxidants
See Ammonium nitrate: Metals
Bromine pentafluoride: Acids, etc.
Nitrogen oxide: Metals
Sulfur dioxide: Metals
See other METALS, PYROPHORIC METALS

4217. Copper chromate oxide

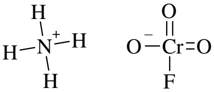
[1308-09-4] **$CrCuO_4.2CuO$**



Hydrogen sulfide
Pascal, 1960, Vol. 13.1, 1025
The gas may ignite on contact with the basic chromate.
See other METAL OXOMETALLATES

4218. Ammonium fluorochromate

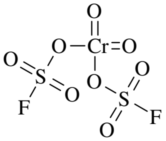
[58501-09-0] **$CrFH_4NO_3$**



Ribas Bernat, J. G., *Ion* (Madrid), 1975, **35**, 573—576
It decomposes violently at 220°C.
See related OXOSALTS OF NITROGENOUS BASES

4219. Chromyl fluorosulfate

[33497-88-0] **$CrF_2O_8S_2$**



Water

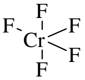
Rochat, W. V. *et al., Inorg. Chem.*, 1969, **8**, 158

Interaction is violent.

See related ACYL HALIDES, OXIDANTS

4220. Chromium pentafluoride

[14884-42-5] **CrF_5**



Bailar, 1973, Vol. 2, 1086

It reacts violently in halogen-exchange and oxidation-reduction reactions.

Phosphorus trichloride

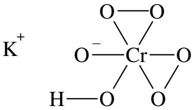
O'Donnell, T. A. *et al., Inorg. Chem.*, 1966, **5**, 1435, 1437

Interaction is violent after slight warming.

See other METAL HALIDES, OXIDANTS

4221. Potassium hydroxyoxodiperoxochromate(1—)

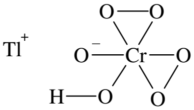
[40330-52-7] (ion) **$CrHKO_6$**



See entry PEROXOCHROMIUM COMPOUNDS

4222. Thallium hydroxyoxodiperoxochromate(1—)

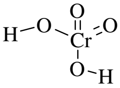
[40330-52-7] (ion) **$CrHO_6Tl$**



See entry PEROXOCHROMIUM COMPOUNDS

4223. Chromic acid

[7738-94-5] **CrH_2O_4**



HCS 1980, 385 (dichromate/sulfuric acid ± added water)

1. Bryson, W. R., *Chem. Brit.*, 1975, **11**, 377
2. Pitt, M. J., *Chem. Brit.*, 1975, **11**, 456
3. Downing, S., *Chem. Brit.*, 1975, **11**, 456
4. Baker, P. B., *Chem. Brit.*, 1975, **11**, 456
5. Kipling, B., *Chem. Brit.*, 1976, **12**, 169
6. Kaufman, J. A., private comm., 1987

A closed bottle of unused potassium dichromate —sulfuric acid mixture exploded after several months in storage [1]. Previous similar incidents were summarised, and the possibility of the bottle having burst from internal pressure of carbon dioxide arising from trace contamination by carbon compounds was advanced [1,2]. Two further reports of incidents within 1 or 2 days of preparation of the mixture were reported [3,4], the latter involving exothermic precipitation of chromium trioxide. Presence of traces of chloride in the dichromate leads to formation of chromyl chloride, which may be unstable [2,5]. The use of other glass-cleaning agents, and non-storage of chromic acid mixtures is again recommended [2]. Used chromic acid cleaning solution was returned to the bottle and capped; it exploded 2—3 mins. later [6].

See other GAS EVOLUTION INCIDENTS

Acetone

MCA Case History No. 1583

During glass cleaning operations, acetone splashed into a beaker used previously to contain potassium dichromate—sulfuric acid mixture and the solvent ignited. Alcohols behave similarly.

Alcohols, Silica gel

Lou, J.-D. *et al., Chem. & Ind.*, 1987, 531—532

Chromic acid adsorbed on silica gel ($CrO_3 : SiO_2 = 3 : 10$) is a mild and safe reagent to oxidise saturated or unsaturated alcohols in carbon tetrachloride to the corresponding aldehydes.

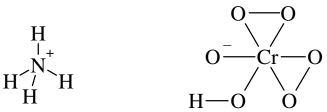
Oxidisable material

MCA Case History No. 1919

A waste plating solution (containing 22% sulfuric acid and 40% w/v of chromium) was being sucked into an acid-disposal tanker. When 500 l had been transferred, a mild explosion in the tanker blew back through the transfer pump and hose. The oxidisable component in the tanker was not identified.

See other INORGANIC ACIDS, OXIDANTS

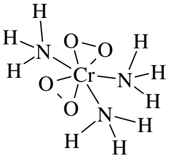
4224. Ammonium hydroxyoxodiperoxochromate(1—)
[40330-52-7] (ion) **CrH_5NO_6**



See entry PEROXOCHROMIUM COMPOUNDS

4225. Triamminediperoxochromium(IV)

[17168-85-3] **$CrH_9N_3O_4$**



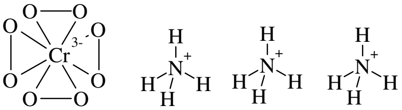
1. Hughes, R. G. *et al., Inorg. Chem.*, 1968, **7**, 882
2. Kauffman, G. B., *Inorg. Synth.*, 1966, **8**, 133

It must be handled with care because it may explode or become incandescent on sudden heating or shock. Heating at 20°/min caused a violent explosion at around 120°C [1]. Preparative and handling precautions have been detailed [2].

See other AMMINECHROMIUM PEROXOCOMPLEXES

4226. Ammonium tetraperoxochromate(3—)

[67165-30-4] **$CrH_{12}N_3O_8$**



Alone, or Sulfuric acid

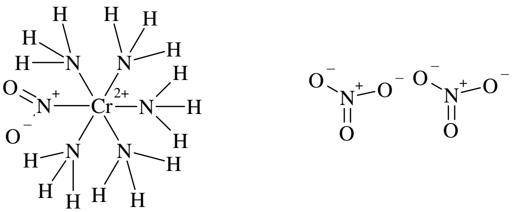
Mellor, 1943, Vol. 11, 356

Explodes at 50°C, on impact, or in contact with sulfuric acid.

See other PEROXOACID SALTS

4227a. Pentaamminenitrochromium(III) nitrate

[31255-94-4] **$CrH_{15}N_8O_8$**



Mellor, 1943, Vol. 11, 477

It explodes on heating, and may be impact-sensitive.

See other AMMINEMETAL OXOSALTS

4227b. Azidopentamminechromium(2+) nitrate (Pentaammineazidochromium(2+) nitrate)

[22317-10-0] (ion) **$CrH_{15}N_{10}O_6$**

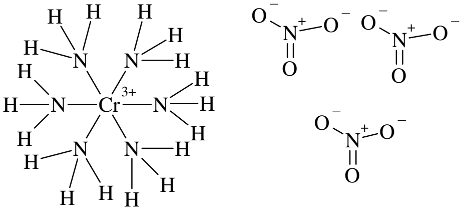
$CrH_{15}N_{10}O_6$

Photolytically explosive

See other AMMINEMETAL NITRATES

4228. Hexaamminechromium(III) nitrate

[15363-28-7] **$CrH_{18}N_9O_9$**

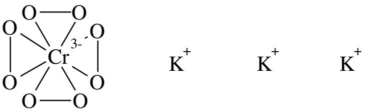


Moderately impact-sensitive, explodes at 263°C.

See entry AMMINEMETAL OXOSALTS (reference 2)

4229. Potassium tetraperoxochromate(3—)

[12331-76-9] **CrK_3O_8**



Alone, or Sulfuric acid

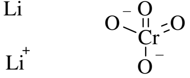
Mellor, 1943, Vol. 11, 356

Not sensitive to impact, but explodes at 178°C or in contact with sulfuric acid. The impure salt is less stable, and explosive.

See other PEROXOACID SALTS

4230. Lithium chromate

[14307-35-8] **$CrLi_2O_4$**



Zirconium

de Boer, H. J. *et al., Z. Anorg. Chem.*, 1930, **191**, 113

During reduction of the chromate to lithium at 450—600°C, a considerable excess of zirconium must be used to avoid explosions.

See other METAL OXOMETALLATES

4231. Chromium nitride

[24094-93-7] **CrN**

Cr^{3+} N^{3-}

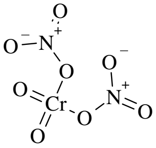
Potassium nitrate

See Potassium nitrate: Chromium nitride

See other NITRIDES

4232. Chromyl nitrate

[16017-38-2] **CrN_2O_8**



Organic materials

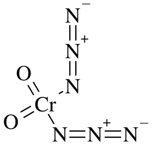
1. Schmeisser, M., *Angew. Chem.*, 1955, **67**, 495
2. Harris, A. D. *et al., Inorg. Synth.*, 1967, **9**, 87

Many hydrocarbons and organic solvents ignite on contact with this powerful oxidant and nitrating agent [1], which reacts like fuming nitric acid in contact with paper, rubber or wood [2].

See related METAL NITRATES

4233. Chromyl azide

[100409-34-5] **CrN_6O_2**



Krauss. H. L. et al., Zeitschrift für Naturforschung, 1962, 17B, 345

A violet solid, sensitive to light and moisure, explodes above 60°C.

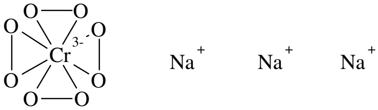
Preparative hazard

See Chromyl chloride: Sodium azide

See related METAL AZIDES

4234. Sodium tetraperoxochromate(3—)

[12206-14-3] **$CrNa_3O_8$**



Mellor, 1943, Vol. 11, 356
It explodes at 115°C.
See other PEROXOACID SALTS

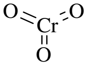
4235. Chromium(II) oxide
[12018-00-7] **CrO**

$$Cr{=}O$$

1. Férée, J., *Bull. Soc. Chim, Fr.*, 1901, *25*, 620
2. Ellern, 1961, 33

The black powder ignites if ground or heated in air [1]. The oxide obtained by oxidation of chromium amalgam is pyrophoric [2].
See other METAL OXIDES, PYROPHORIC MATERIALS, REDUCANTS

4236. Chromium trioxide
[1333-82-0] **CrO_3**



(*MCA SD-52*, 1944); *FPA H48*, 1976; *HCS 1980*, 315

1. Baker, W., *Chem. & Ind.*, 1956, 280
2. Goertz, A., *Arbeitschutz*, 1935, 323

Presence of nitric acid or nitrates in chromium trioxide may cause oxidation reactions to accelerate out of control, possibly owing to formation of chromyl nitrate. Samples of the oxides should be tested by melting before use, and those evolving oxides of nitrogen should be discarded [1]. A closed container of the pure oxide exploded violently when laid down on its side. This was attributed to unsuspected contamination of the container [2].
See Chromyl nitrate

Acetic acid MRH 2.22/18

1. Anon., *BCISC Quart. Safety Summ.*, 1966, **37**, 30
2. Anon., *Sichere Chemiearb.*, 1987, **39**, 70

An explosion occurred during initial heating of a large volume of glacial acetic acid being treated with chromium trioxide. This was attributed to violent interaction of solid chromium trioxide and liquid acetic acid on a hot, exposed steam coil, and subsequent initiation of an explosive mixture of acetic acid vapour and air. The risk has been obviated by using a solution of dichromate in sulfuric acid as oxidant, in place of the trioxide. The sulfuric acid is essential, as the solid dichromate, moist with acetic acid obtained by evaporating an acetic acid solution to near-dryness, will explode [1]. Use of a mixture of chromium trioxide and acetic acid as an oxidant shattered a glass reaction vessel [2].
See Butyric acid, below
See other GLASS INCIDENTS

Acetic anhydride MRH 2.38/16

1. Dawber, J. G., *Chem. & Ind.*, 1964, 973
2. Bretherick, L., *Chem. & Ind.*, 1964, 1196
3. Baker, W., *Chem. & Ind.*, 1956, 280
4. Eck, C. R. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 865
5. *MCA Guide*, 1972, 297

A literature method for preparation of chromyl acetate by interaction of chromium trioxide and acetic anhydride was modified by omission of cooling and agitation. The warm mixture exploded violently when moved [1]. A later publication emphasised the need for cooling, and summarised several such previous occurrences [2]. An earlier reference attributes the cause of chromium trioxide—acetic anhydride oxidation mixtures going out of control to presence of nitric acid or nitrates in the chromium trioxide, and a simple test to check this point is given [3]. Mixtures used as a reagent for the remote oxidation of carboxylic esters are potentially explosive, and must be made up and used at below 25°C under controlled conditions [4]. An attempt to purify the anhydride by warming with 2% w/v of trioxide led to an explosion at 30°C [5].

Acetic anhydride, 3-Methylphenol

Thorne, J. G., private comm., 1978

Addition of the oxide in portions to the reaction mixture (for preparation of 3-hydroxybenzaldehyde or its acetate) at 75—80°C proceeded smoothly, but the final portion caused a large exotherm leading to eruption of the flask contents.

Acetic anhydride, Tetrahydronaphthalene

Peak, D. A., *Chem. & Ind.*, 1949, 14

Use of an anhydride solution of the trioxide to prepare tetralone caused a vigorous fire. This was attributed to use of the more hygroscopic granular trioxide, which is less preferable than the flake type.

Acetone MRH 2.59/10

Delhez, R., *Chem. & Ind.*, 1956, 931

The use of chromium trioxide to purify acetone is hazardous, ignition on contact occurring at ambient temperature. Methanol behaves similarly when used to reduce the trioxide in preparing hexaaquachromium(III) sulfate.

Acetylene

Grignard, 1935, Vol. 3, 167

Acetylene is oxidised violently.

Alcohols MRH Ethanol 2.55/10

1. Newth, F. H. *et al., Chem. & Ind.*, 1964, 1482
2. Neumann, H., *Chem. Eng. News*, 1970, **48**(24), 4
3. *491M*, 1975, 126
4. Kishore, K., *Def. Sci. J.*, 1978, **28**, 13—14

When methanol was used to rinse a pestle and mortar which had been used to grind coarse chromium trioxide, immediate ignition occurred due to vigorous oxidation of the solvent. The same occurred with ethanol, 2-propanol, butanol and cyclohexanol. Water is a suitable cleaning agent for the trioxide [1]. For oxidation of *sec*-alcohols in

DMF, the oxide must be finely divided, as lumps cause violent local reaction on addition to the solution [2]. Use of methanol to reduce the Cr(VI) oxide to a Cr(III) derivative led to an explosion and fire [3]. The ignitability of the butanols decreases from n- through *sec*- to *tert*-butanol [4].
See Dimethylformamide, below

Alkali metals MRH Potassium 1.46/23, sodium 3.39/21
Mellor, 1943, Vol. 11, 237
Sodium or potassium reacts with incandescence.

Ammonia MRH Gas 2.51/15, solution 1.63/26
1. Mellor, 1943, Vol. 11, 233
2. Pascal, 1959, Vol. 14, 215

Gaseous ammonia leads to incandescence [1], and the aqueous solution is oxidised very exothermally [2].

Arsenic
Mellor, 1943, Vol. 11, 234
Interaction is incandescent.

Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.

Butyric acid
Wilson, R. D., *Chem. & Ind.*, 1957, 758
A mixture of chromium trioxide and butyric acid became incandescent on heating to 100°C.
See Acetic acid, above

Chlorine trifluoride
See Chlorine trifluoride: Chromium trioxide

Chromium(II) sulfide
Mellor, 1943, Vol. 11, 430
Interaction causes ignition.

Dimethylformamide MRH 2.64/11
1. Neumann, H. *Chem. Eng. News*, 1970, **48**(28), 4
2. Heathcock, C. H., *Chem. Eng. News*, 1981, **59**(8), 9

During oxidation of a *sec*-alcohol to ketone in cold DMF solution, addition of solid trioxide caused ignition. Addition of lumps of trioxide was later found to cause local ignition on addition to ice-cooled DMF under nitrogen [1]. Addition of 2 g of chromium trioxide to 18 ml of solvent to form a 10 wt% solution caused immediate ignition and ejection of the flask contents [2].
See Dimethylformamide: Oxidants

1,3-Dimethylhexahydropyrimidone
Mukhopadhyay, T. *et al., Helv. Chim. Acta*, 1982, **65**, 386 (footnote 9)
Contact of the trioxide with the aprotic amide solvent (‘dimethylpropyleneurea’) is always explosive, with fire, whereas this only occurs with hexamethylphosphoramide

(below) if the oxide is previously crushed. However the former is much less toxic than the latter solvent.

Ethylene glycol
See Ethylene glycol: Oxidants

Glycerol MRH 2.38/17
Pieters, 1957, 30
Interaction is violent; the mixture may ignite owing to oxidation of the trihydric alcohol, which is viscous and unable to dissipate the exotherm.
See Glycerol: Oxidants

Hexamethylphosphoramide
Cardillo, G. *et al., Synthesis*, 1976, **6**, 394—396
Stirring chromium trioxide (added in small portions) with the unheated solvent leads to the formation of a complex useful for oxidising alcohols to carbonyl derivatives. The trioxide must not be crushed before being added to the solvent, because violent decomposition may then occur.
See 1,3-Dimethylhexahydropyrimidone, above

Hydrazine MRH 3.01/19
See Hydrazine: Oxidants (reference 2)

Hydrogen sulfide MRH 2.05/12
Mellor, 1943, Vol. 11, 232
Contact with the heated oxide causes incandescence.

Organic materials, or Solvents MRH values below references show % of organic

1. Leleu, *Cahiers*, 1976, (83), 286—287
2. Fawcett, H. H., *Ind. Eng. Chem.*, 1959, **51**(4), 90A
3. Mikhailov, V., *Chem. Abs.*, 1960, **54**, 23331f
4. Mellor, 1943, Vol. 11, 235

MRH Aniline 2.59/8, diethyl ether 2.59/8, hexane 2.46/6, phenol 2.51/9, toluene 2.55/7

Combustible materials may ignite or explode on contact with the oxide. A few drops of oil which fell into a container of the oxide led to an explosion which produced fatal burns [1]. If a few drops of an organic solvent (acetone, 2-butanone, ethanol) contact solid chromium trioxide, a few seconds' delay ensues while some of the oxidant attains the critical temperature of 330°C. Then combustion occurs with enough vigour to raise a fire-ball several feet, and spattering also occurs [2]. Possible ignition hazards were studied for a range of 60 organic liquids and solids in contact with the solid oxide. Hot liquids were added to the oxide; solids were covered with a layer of the oxide. The most dangerous materials were methanol, ethanol, butanol, isobutanol, acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, acetic acid, pelargonic acid, ethyl acetate, isopropyl acetate, pentyl acetate, diethyl ether, methyldioxane, dimethyldioxane, acetone and benzylethylaniline. Other materials evolved heat, especially in presence of water. Segregation in storage or transport is essential [3]. Benzene ignites in contact with the powdered oxide [4].

See 1,3-Dimethylhexahydropyrimidone, or Dimethylformamide, or Glycerol, or Hexamethylphosphoramide, all above

Other reactants

Yoshida, 1980, 354—355

MRH values calculated for 28 combinations, largely with oxidisable materials, are given.

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

Phosphorus MRH (Yellow) 3.68/16

Moissan, H., *Ann. Chim. Phys. [6]*, 1885, **5**, 435

Phosphorus and the molten trioxide react explosively.

Potassium hexacyanoferrate(III) MRH 2.59/25

1. Anon., *BCISC Quart. Safety Summ.*, 1965, **36**(144), 55
2. Cardillo, P. *Chem. Ind. (Milan)*, **74**(6), 441

Mixtures of the ferrate ('ferricyanide') and chromium trioxide explode and inflame when heated above 196°C. Friction alone is sufficient to ignite violently the mixture when ground with silver sand. An account of an actual accident of this type is given [2].

See other FRICTIONAL INITIATION INCIDENTS

Pyridine MRH 2.63/92

1. Dauben, W. G. *et al., J. Org. Chem.*, 1969, **34**, 3587
2. Poos, G. I. *et al., J. Amer. Chem. Soc.*, 1953, **75**, 427
3. Collins, J. C. *et al., Org. Synth.*, 1972, **52**, 7
4. Ratcliffe, R. *et al., J. Org. Chem.*, 1970, **35**, 4001
5. Stensio, K. E., *Acta Chem. Scand.*, 1971, **25**, 1125
6. *MCA Case History No. 1284*

During preparation of the trioxide—pyridine complex (a powerful oxidant), lack of really efficient stirring led to violent flash fires as the oxide was added to the pyridine at —15 to —18°C. Reversed addition of pyridine to the oxide is extremely dangerous [1], ignition usually occurring [2]. A later preparation specifies temperature limits of 10—20°C to avoid an excess of unreacted trioxide [3]. A safe method of preparing the complex in solution has been described [4], and preparation and use of solutions of the isolated complex in dichloromethane [3] or acetic acid [5] have been detailed. The Case History gives further information on preparation of the complex. Solution of the oxide is not smooth; it first swells, then suddenly dissolves in pyridine with an exotherm. This hazard may be eliminated without loss of yield by dissolving the trioxide in an equal volume of water before adding it to 10 volumes of pyridine. Pulverising chromium trioxide before use is not recommended, as this increases its rate of reaction with organic compounds to a hazardous level [6].

See Oxodiperoxopyridinechromium *N*-oxide

Selenium

Mellor, 1943, Vol. 11, 233

Interaction is violent.

Silica gel, Carbon monoxide

Foster, D. F. *et al., Inorg. Synth.*, 1997, **31**, 29

The oxide, absorbed onto silica gel and then reduced with carbon monoxide,may become pyrophoric

Sodium MRH 3.39/21

See Sodium: Metal oxides

See other REDOX REACTIONS

Sodium amide

Mellor, 1943, Vol. 11, 234

Grinding a mixture leads to violent reaction.

Sulfur MRH 1.76/14

Mellor, 1943, Vol. 11, 232

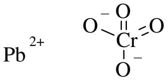
A mixture ignites on warming.

See other METAL OXIDES, OXIDANTS

See related ACID ANHYDRIDES

4237. Lead chromate

[7758-97-6] **CrO_4Pb**



HCS 1980, 587

Aluminium, Dinitronaphthalene

Nagaishi, T. *et al., Chem. Abs.*, 1977, **86**, 59602

The considerable energy released by the mixture derives from chromate-catalysed exothermic decomposition of the nitro compound, coupled with a thermite-type reaction of the aluminium and chromate. It is useful for cracking concrete.

Azo-dyestuffs

Anon., *Loss Prev. Bull.*, 1978, (022), 117

Under certain conditions, dry mixtures of lead chromate pigments with the azo-dyes 1-(2’,4’-dinitrobenzeneazo)-2-hydroxynaphthalene (dinitroaniline orange) or 1-(4’-chloro-2’-nitrobenzeneazo)-2-hydroxynaphthalene (chlorinated para-red) may lead to violent explosions during mixing/blending operations.

See N, N”-Dichlorobis(2,4,6-trichlorophenyl)urea: 1-*p*-Nitrobenzeneazo-2-naphthol

Iron(III) hexacyanoferrate(4—)

1. Anon., *Chem. Processing*, 1967, **30**, 118
2. Twitchett, H. J., *Chem. Brit.*, 1977, **13**, 437

During grinding operations, the intimate mixture of pigments was ignited by a spark and burned fiercely [1]. Spontaneous ignition of Brunswick Green pigment (which also contains lead sulfate) soon after grinding was not uncommon, and similar incidents had led to the loss of ships with cargoes of Prussian Blue or Brunswick Green in wooden casks [2].

See Azo-dyestuffs, above

See other SELF-HEATING AND IGNITION INCIDENTS

Sulfur

Jackson, H., *Spectrum*, 1969, **7**(2), 82

The mixture is pyrophoric.

Tantalum

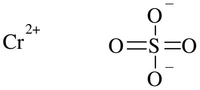
Sarawadekar, R. G. *et al., Thermochim. Acta*, 1983, **70**, 133

The mixture is a pyrotechnic composition.

See other METAL OXOMETALLATES, OXIDANTS

4238. Chromium(II) sulfate

[13825-86-0] **CrO_4S**



Water

1. van Bemmelen, J. M., *Rec. Trav. Chim.*, 1887, **6**, 202—204
2. Bailar, 1973, Vol. 3, 657—658

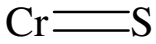
Crystals of the heptahydrate, damp with surplus water, were sealed into a glass tube and stored in darkness, and after a year the tube exploded. This was attributed to the pressure of hydrogen liberated by reduction of water by the chromium(II) salt [1]. More recent information [2] confirms this hypothesis.

See CHROMIUM(II) CHLORIDE

See other METAL OXONON-METALLATES, REDUCANTS

4239. Chromium(II) sulfide

[12018-06-3] **CrS**



Chromium trioxide

See Chromium trioxide: Chromium(II) sulfide

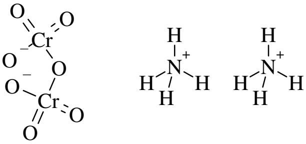
Fluorine

See Fluorine: Sulfides

See other METAL SULFIDES

4240. Ammonium dichromate

[7789-09-5] **$Cr_2H_8N_2O_7$**



(*MCA SD-45*, 1952); *HCS 1980*, 143

1. Mellor, 1943, Vol. 11, 324
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
3. Anon., *Chem. Eng. News*, 1986, **64**(4), 6
4. Bretherick, L., *Chem. Eng. News*, 1986, **64**(22), 4

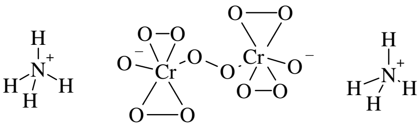
Thermal decomposition of the salt (which is of zero oxygen balance) is initiated by locally heating to 190°C, and flame and sparks spread rapidly through the mass, and if confined, it may become explosive [1]. Under close confinement, the deflagrating salt shows the extraordinarily high rate of pressure increase of 68 kbar/s, attaining a final pressure of 510 bar in about 10 ms, and further study of its deflagration and homogeneous decomposition under confinement have been reported [2]. Energy of decomposition (in range 230—260°C) was measured as 0.76 kJ/g by DSC, and T_{ait24} was determined as 96°C by adiabatic Dewar tests, with an apparent energy of activation of 112 kJ/mol. Following a report of an explosion during heated vacuum drying of a 1 t quantity of the salt [3], attention was drawn [4] to the extreme potential hazard involved in heating the salt under confinement.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION
See other DEFLAGRATION INCIDENTS

Ethylene glycol
See Ethylene glycol: Oxidants
See other DICHROMATE SALTS OF NITROGENOUS BASES

4241. Ammonium pentaperoxodichromate(2—)

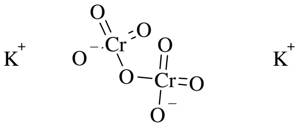
[ ] **$Cr_2H_8N_2O_{12}$**



Brauer, 1965, Vol. 2, 1392
It explodes at 50°C.
See other PEROXOACID SALTS

4242. Potassium dichromate

[7778-50-9] **$Cr_2K_2O_7$**



FPA H43, 1976

Boron, Silicon

See Boron: Dichromates, etc.

Ethylene glycol MRH 1.46/11

Yoshida, T., private comm., 1982

Mixing of equal weights at ambient temperature is uneventful, but at 100° an exotherm of 170°C occurs.

Hydrazine MRH 1.59/99+

Mellor, 1943, Vol. 11, 234

Explosive interaction.

See Hydrazine: Oxidants (reference 2)

Hydroxylamine MRH 3.85/99+

See Hydroxylamine: Oxidants

Iron MRH 0.42/34

Laye, P. G. *et al., Thermochim. Acta*, 1980, **39**, 3567—359

Pyrotechnic mixtures (1:1 wt) attained a maximum temperature of about 1090°C on ignition.

See Tungsten, below

Sulfuric acid

See Chromic acid

Tungsten

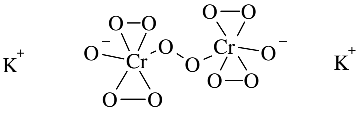
Boddington, T. *et al., Combust. Flame*, 1975, **24**, 137—138

Combustion of a pyrotechnic mixture of the two materials (studied by DTA and temperature profile analysis) attains a temperature of about 1700°C in 0.1—0.2 s.

See other METAL OXOMETALLATES, OXIDANTS

4243. Potassium pentaperoxodichromate

[ ] **$Cr_2K_2O_{12}$**



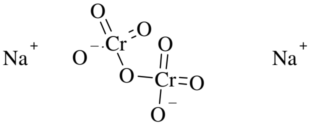
Mellor, 1943, Vol. 11, 357; Sidgwick, 1950, 1007

The powdered salt explodes above 0°C.

See other PEROXOACID SALTS

4244. Sodium dichromate

[10588-01-9] **$Cr_2Na_2O_7$**



HCS 1980, 838

Acetic acid, 2-Methyl-2-pentenal

Nolan, 1983, Case history 73

2-Methyl-2-pentenal was oxidised to the acid in a process involving addition over a period into a mixture of acetic acid and sodium dichromate at 50°C. Addition of the aldehyde, effected by sucking it into the reactor by application of vacuum, was entrusted to an inexperienced operator, but was apparently too fast and the exotherm led to a runaway and eruption of the reactor contents.

Acetic anhydride MRH 1.84/13

Marszalek, G., private comm., 1973

Addition of the dehydrated salt to acetic anhydride caused an exothermic reaction which accelerated to explosion. Presence of acetic acid (including that produced by hydrolysis of the anhydride by the hydrate water) has a delaying effect on the onset of violent reaction, which occurs where the proportion of anhydride to acid (after hydrolysis) exceeds 0.37:1, with an initial temperature above 35°C. Mixtures of dichromate (30 g) with anhydride—acid mixtures (70 g, to give ratios of 2:1, 1:1, 0.37:1) originally at 40°C accelerated out of control after 18, 43 and 120 min, to 160, 155 and 115°C, respectively.

See other INDUCTION PERIOD INCIDENTS

Boron, Silicon

See Boron: Dichromates, etc.

Ethanol, Sulfuric acid

1. Annable, E. H., *School Sci. Rev.*, 1951, **32**(117), 249
2. Anon., *Education in Science*, 1990, (140), 30

During preparation of acetic acid by acid dichromate oxidation of ethanol according to a published procedure, minor explosions occurred on two occasions after refluxing had been discontinued. This possibly may have involved formation of acetaldehyde (which has an AIT of 140°C) and ingress of air into the reaction vessel as it cooled [1]. Runaway reactions during small scale oxidation of ethanol have apparently been experienced by many teachers, poor initial mixing or starting too cool may be the cause [2].

See 2-Propanol, Sulfuric acid, below

Hydrazine

Mellor, 1943, Vol. 11, 234

Interaction is explosive.

See Hydrazine: Oxidants

Hydroxylamine
See Hydroxylamine: Oxidants

Organic residues, Sulfuric acid MRH Acetone 1.97/8
1. *HCS 1980*, 385
2. Bradshaw, J. R., *Process Biochem.*, 1970, **5**(11), 19
3. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 95

The well-known ‘chromic acid mixture’ of dichromate and sulfuric acid [1] for cleaning glassware is by design a powerful oxidant, and contact with large amounts of tarry or other organic residues in process vessels should be avoided as it may lead to a violent reaction. Further, if solvents are first used to clean glassware roughly before acid treatment, traces of readily oxidisable solvents must be removed before adding the oxidant mixture. In many cases treatment with a properly formulated detergent will ensure adequate cleanliness and avoid possible hazard [2]. Addition of 1 l of oxidant mixture to a vessel containing residues of acetone or similar solvent led to a violent exothermic reaction [3].
See Chromic acid: Acetone
See also Chromium trioxide: Acetic acid

Other reactants
Yoshida, 1980, 177
MRH values calculated for 16 combinations with oxidisable materials are given.

2-Propanol, Sulfuric acid
Cochrane, A., private comms., 1982, 1983
An established school preparation of 2-propanone (acetone) involves the small-scale (and rather exothermic) oxidation of the alcohol with dichromate(VI). It was observed in several laboratories that when the acidified dichromate solution was added to the alcohol in small portions (1—2 cc) rather than dropwise as specified, small sparks or incandescent particles were produced which sometimes survived long enough to escape from the neck of the flask. This also happened if the alcohol and/or the oxidant solution were diluted with extra water, with old or new samples of alcohol, and if air were displaced from the flask by carbon dioxide. It is therefore important not to exceed the specified dropwise rate of addition of oxidant solution. It is very unusual for glowing particles to be produced from a homogeneous liquid reaction system.
See Ethanol, Sulfuric acid, above

Sulfuric acid, Trinitrotoluene
Clarke, H. T. *et al., Org. Synth.*, 1941, Coll. Vol. 1, 543—544
During oxidation of TNT in sulfuric acid to trinitrobenzoic acid, stirring of the viscous reaction mixture must be very effective to prevent added portions of solid dichromate causing local ignition.
See other AGITATION INCIDENTS, METAL OXOMETALLATES, OXIDANTS, SELF-HEATING AND IGNITION INCIDENTS

4245. Chromium(III) oxide

[1308-38-9] **Cr_2O_3**

Cr^{3+} Cr^{3+} O^{2-} O^{2-} O^{2-}

Chlorine trifluoride
See Chlorine trifluoride: Metals, etc.

Copper oxide
See COPPER CHROMITE CATALYST

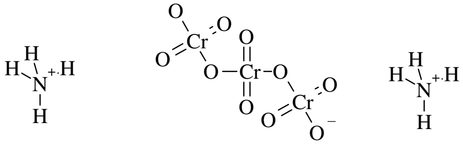
Lithium
See Lithium: Metal oxides

Nitroalkanes
See NITROALKANES: METAL OXIDES

Rubidium acetylide
See Rubidium acetylide: Metal oxides
See other METAL OXIDES

4246. Ammonium trichromate(2—)

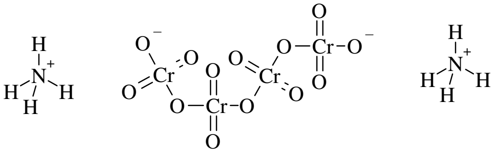
[34390-97-1] **$Cr_3H_8N_2O_{10}$**



Mellor, 1943, Vol. 11, 349
It explodes at 190°C.
See other OXOSALTS OF NITROGENOUS BASES

4247. Ammonium tetrachromate(2—)

[54153-83-2] **$Cr_4H_8N_2O_{13}$**



Mellor, 1943, Vol. 11, 352
It decomposes suddenly at 175°C.
See other OXOSALTS OF NITROGENOUS BASES

4248. Caesium

[7440-46-2] **Cs**

Cs

1. Mellor, 1941, Vol. 2, 468; 1963, Vol. 2, Suppl. 2.2, 2291
2. Pepmiller, P. L. *et al., Rev. Sci. Instr.*, 1985, **56**, 1832—1833

It ignites immediately in air or oxygen [1]. A simple device to open glass vials of caesium and dispense the contents safely gives a good margin of safety to the user [2].

Acids

Pascal, 1957, Vol. 3, 94

Most acids react violently, even when anhydrous.

Halogens

Gibson, 1969, 8

Interaction at ambient temperature is violent with all halogens.

Non-metals

Pascal, 1957, Vol. 3, 94

Interaction with sulfur or phosphorus attains incandescence.

Water

1. Mellor, 1941, Vol. 2, 468; 1963, Vol. 2, Suppl. 2.2, 2328
2. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633—636

Caesium reacts very violently with cold water and the evolved hydrogen ignites [1]. The reactivity of caesium and other alkali metals with water has been discussed in detail [2].

See other METALS, PYROPHORIC METALS

4249. Caesium fluoride

[13400-13-0] **CsF**

$Cs^+ \quad F^-$

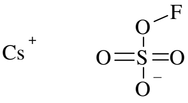
Benzenediazonium tetrafluoroborate, Difluoramine

See Difluoramine: Benzenediazonium tetrafluoroborate, etc.

See other METAL HALIDES

4250. Caesium fluoroxysulfate

[70806-67-6] **$CsFO_4S$**



$Cs^+ \quad {}^-O{-}S(=O)_2{-}O{-}F$

Appelman, E. H., *Inorg. Synth.*, 1986, **24**, 22—23

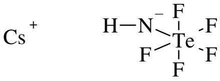
Caesium fluorooxysulfate is thermodynamically unstable. Mild detonations have occurred occasionally during handling of 100 mg portions of salt, usually when deliberate or violent crushing or scraping occurred. It is likely that detonations were brought about by surface impurities on containers or spatulae. Amounts of 10—20 g have been used routinely over several years without detonations, though great care, shields and gloves were always used. It is also a powerful oxidant and reacts violently with organic solvents, including dimethylformamide, dimethyl sulfoxide, ethylene dichloride and pyridine.

See Rubidium fluoroxysulfate

See other ACYL HYPOHALITES, OXIDANTS

4251. Caesium pentafluorotelluramide

[42081-47-0] **CsF_5HNTe**



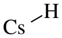
Seppelt, K., *Inorg. Chem.*, 1973, **12**, 2838

Heating must be avoided during the preparation or subsequent drying, as occasional explosions occurred. It exploded immediately upon laser irradiation for Raman spectroscopy.

See other IRRADIATION DECOMPOSITION INCIDENTS, N-METAL DERIVATIVES

4252. Caesium hydride

[13772-47-9] **CsH**



Oxygen

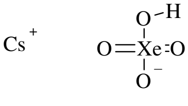
Gibson, 1969, 76

The unheated hydride ignites in oxygen.

See other METAL HYDRIDES

4253. Caesium hydrogen xenate

[73378-56-0], Sesquihydrate **$CsHO_4Xe$**



Alone, or Alcohols

Jaselskis, B. *et al., J. Amer. Chem. Soc.*, 1966, **88**, 2150; 1969, **91**, 1874

It is unstable to friction, thermal or mechanical shock, and may explode on contact with alcohols.

See other XENON COMPOUNDS

4254. Caesium amide

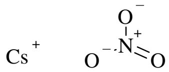
[22205-57-8] **CsH_2N**

Pez, G. P. *et al., Pure Appl. Chem.*, 1985, **57**, 1917—1926
Caesium amide is extremely pyrophoric and must be handled in an atmosphere virtually free from oxygen and moisture (each below 5 ppm).

Water
Mellor, 1940, Vol. 8, 256
Interaction is incandescent in presence of air.
See other INORGANIC BASES, N-METAL DERIVATIVES

4255. Caesium nitrate

[7789-18-6] **$CsNO_3$**

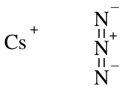


Xenon hexafluoride
See Xenon hexafluoride: Caesium nitrate

Xenon tetrafluoride
See Xenon tetrafluoride: Caesium nitrate
See other METAL NITRATES

4256. Caesium azide

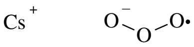
[22750-57-8] **CsN_3**



Sulfur dioxide
Kennet, F. A. *et al., J. Chem. Soc., Dalton Trans.*, 1982, 853
The azide ignites in contact with sulfur dioxide at ambient temperature.
See other METAL AZIDES

4257. Caesium trioxide (Caesium ozonide)

[12053-67-7] **CsO_3**



Water
Whaley, T. P. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 79

Reaction of caesium or potassium ozonides with water or aqueous acids is violent, producing oxygen and flashes of light.
See other METAL OXIDES

4258. Caesium oxide

[20281-00-9] **Cs_2O**

$$Cs^{+} \quad Cs^{+} \quad O^{2-}$$

Ethanol
Pascal, 1957, Vol. 3, 104
Contact of a little alcohol with the oxide may ignite the solvent.

Halogens, or Non-metal oxides
Mellor, 1941, Vol. 2, 487
Above 150—200°C, incandescence occurs with fluorine, chlorine or iodine. In presence of moisture, contact at ambient temperature with carbon monoxide or carbon dioxide causes ignition, while dry sulfur dioxide causes incandescence on heating.

Water
Pascal, 1957, Vol. 3, 104
Incandescence on contact.
See other METAL OXIDES

4259. Caesium selenide

[31052-46-7] **Cs_2Se**

$$Cs^{+} \quad Cs^{+} \quad Se^{2-}$$

Sidgwick, 1950, 92
When warm it ignites in air.
See related METAL SULFIDES

4260. Caesium nitride

[12134-29-1] **Cs_3N**

$$Cs^{+} \quad Cs^{+} \quad Cs^{+} \quad N^{3-}$$

Alone, or Chlorine, or Non-metals
Mellor, 1940, Vol. 8, 99
It burns in air, and is readily attacked by chlorine, phosphorus or sulfur.
See other NITRIDES

4261. Copper

[7440-50-8] **Cu**

Cu

Acetylenic compounds

See ACETYLENIC COMPOUNDS: Metals

Aluminium, Sulfur

See Aluminium: Copper, Sulfur

3-Bromopropyne

See 3-Bromopropyne: Metals

Complexing agents, Water

Shah, I. U., *Chem. Eng. News*, 1991, **69**(30), 2

A bottle of 'cuprous chloride' solution prepared by standing cupric chloride in strong hydrochloric acid over excess copper burst on standing. (Editor's comments) In the presence of some complexing agents, copper can react with aqueous media to form hydrogen. Slow pressurisation by this means explains the above explosion. The metal is also known to dissolve in cyanides and some amine solutions.

Dimethyl sulfoxide, Trichloroacetic acid

See Dimethyl sulfoxide: Copper, Trichloroacetic acid

Ethylene oxide

See Ethylene oxide (reference 3)

Lead azide

See Lead(II) azide: Copper

Other reactants

Yoshida, 1980, 243

MRH values calculated for 11 combinations with oxidants are given.

Oxidants MRH Sodium chlorate 2.0/36

Mellor, 1941, Vol. 2, 310

Mixtures of finely divided copper with chlorates or iodates explode on friction, shock or heating.

See Ammonium nitrate: Metals
Chlorine trifluoride: Metals, etc.
Chlorine: Metals
Fluorine: Metals
Hydrazinium nitrate: Alone, or Metals
Hydrogen sulfide: Metals
Potassium dioxide: Metals
Sulfuric acid: Copper

Water

Zyszkowski, W., *Int. J. Heat Mass Transf.*, 1976, **19**, 849—868

The vapour explosion which occurs when liquid copper is dumped into water has been studied.

See MOLTEN METAL EXPLOSIONS

See other METALS

4262. Copper—zinc alloys

[12019-27-1] **Cu—Zn**

Cu—Zn

Alkyl halides

See DIALKYLZINCS

Diiodomethane, Ether

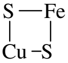
1. Foote C. S., private comm., 1965
2. Repic, O. *et al., Tetrahedron Lett.*, 1982, **23**, 2729—2732

Lack of cooling during preparation of the Simmons-Smith organozinc reagent caused the reaction to erupt. The possibly pyrophoric nature of organozinc compounds and the presence of ether presents a severe fire hazard [1]. An alternative, safer method of activating the zinc for the reaction involves use of ultrasonic irradiation rather than the copper—zinc couple [2].

See other ALLOYS

4263. Copper iron(II) sulfide

[12015-76-8] **$CuFeS_2$**



Ammonium nitrate

See Ammonium nitrate: Copper iron(II) sulfide

Water

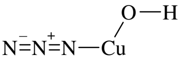
Gribin, A. A., *Chem. Abs.*, 1943, **37**, 1272_8

A large dump of copper pyrites ore ignited after heavy rain. The thick layer (6—7 m) and absence of ventilation were contributory factors to the accelerating aerobic oxidation which finally led to ignition.

See other METAL SULFIDES, SELF-HEATING AND IGNITION INCIDENTS

4264. Copper(II) azide hydroxide

[22887-15-6] **$CuHN_3O$**



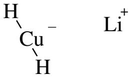
Cirulis, A., *Z. Anorg. Chem.*, 1943, **251**, 332—334

It exploded at 203°C or on impact. The dimeric double salt is similarly sensitive.

See related METAL AZIDES

4265. Lithium dihydrocuprate

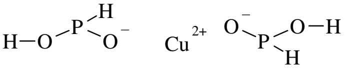
[53201-99-3] **CuH_2Li**



Ashby, E. C. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 157—158
The solid is highly pyrophoric, but stable as a slurry in ether at ambient temperature.
See other COMPLEX HYDRIDES

4266. Copper(II) phosphinate

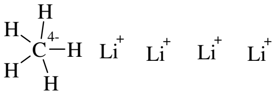
[34461-68-2] **$CuH_4O_4P_2$**



Mellor, 1940, Vol. 8, 883: 1971, Vol. 8, Suppl. 3, 623
The solid suddenly explodes at about 90°C, and forms impact-sensitive priming mixtures.
See other METAL PHOSPHINATES, REDOX COMPOUNDS

4267a. Lithium pentahydrocuprate(4—)

[64010-65-7] **CuH_5Li_4**



Ashby. E. C. *et al., J. Org. Chem.*, 1978, **43**, 187
Of a series of lithium hydrocuprates Li_nCuH_{n+1} (n = 1—5), only the title compound (when solvated with THF) appeared a more powerful reducant than lithium tetrahydroaluminate. Safety precautions similar to those adopted for the complex aluminium hydride seem appropriate.
See other COMPLEX HYDRIDES

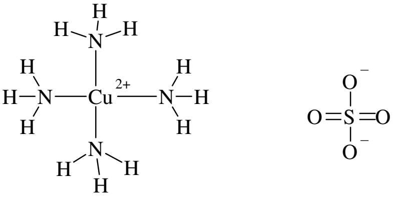
4267b. Azidotriamminecopper(1+) nitrate (Triammineazidocopper(1+) nitrate)

[148331-08-2] (ion) **$CuH_9N_7O_3$**

$CuH_9N_7O_3$

Photolytically explosive
See other AMMINEMETAL NITRATES

4268. Tetraamminecopper(II) sulfate
[14283-05-7] **$CuH_{12}N_4O_4S$**

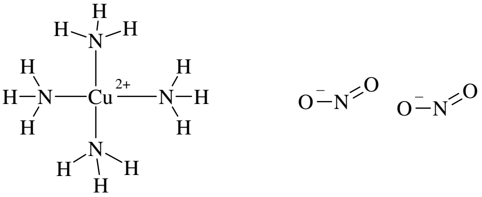


Iodine

See Iodine: Tetraamminecopper(II) sulfate

See other AMMINEMETAL OXOSALTS

4269. Tetraamminecopper(II) nitrite
[39729-81-2] **$CuH_{12}N_6O_4$**

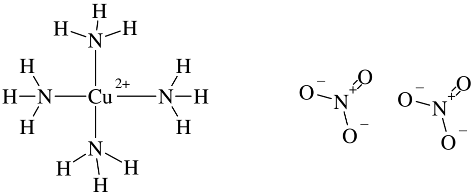


Mellor, 1940, Vol. 8, 480

The salt is nearly as shock-sensitive as picric acid. When pure it does not explode on heating, but traces of nitrate cause explosive decomposition.

See other AMMINEMETAL OXOSALTS

4270. Tetraamminecopper(II) nitrate
[31058-64-7] **$CuH_{12}N_6O_6$**

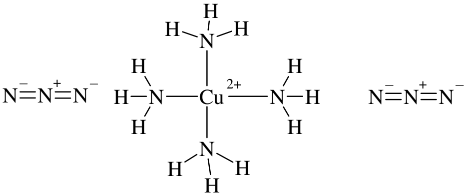


Explodes at 330°C, high impact-sensitivity.

See entry AMMINEMETAL OXOSALTS (reference 2)

4271. Tetraamminecopper(II) azide

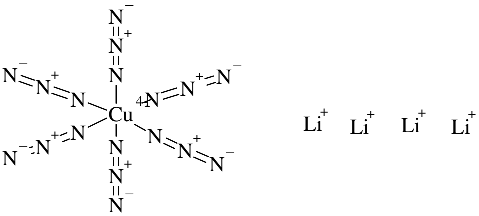
[70992-03-9] **$CuH_{12}N_{10}$**



Mellor, 1940, Vol. 8, 348; 1967, Vol. 8, Suppl.2, 26
Explosive on heating or impact.
See related METAL AZIDES

4272. Lithium hexaazidocuprate(4—)

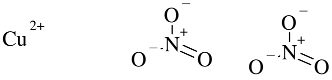
[ ] **$CuLi_4N_{18}$**



Urbanski, 1967, Vol. 3, 185
It is, like copper(II) azide, an exceptionally powerful initiating detonator, containing 61.5% of nitrogen.
See other HIGH-NITROGEN COMPOUNDS
See related METAL AZIDES

4273. Copper(II) nitrate

[3251-23-8] [10031-43-3]; [13478-38-1] hydrates **CuN_2O_6**



HCS 1980, 336

Priestley J., *Experiments and Observations on Different Kinds of Air*, 1790, 3, 203, Birmingham
Although the anhydrous nitrate is relatively stable and can be distilled under partial pressure, as is remarked in most modern text books, these do not tell that the hydrate actually obtainable by purchase or by normal preparations is among the least stable and most oxidising of main valence nitrates. It was early observed that paper contaminated with it ignited easily [1].

Acetic anhydride MRH 3.56/26

See Acetic anhydride: Metal nitrates

Ammonia, Potassium amide

Sorbe, 1968, 80

Interaction gives an explosive precipitate containing the Cu(I) derivatives Cu_3N, $Cu_3N \, . \, n NH_3$, Cu_2NH, $CuNK_2 \, . \, NH_3$.

Ammonium hexacyanoferrate(II)

1. Wolski, J. *et al., Z. Chem.*, 1973, **13**, 95—97
2. Wolski, J. *et al., J. Therm. Anal.*, 1973, **5**, 67

At 220°C interaction is explosive in wet mixtures [1], or in dry mixtures if the nitrate is in excess [2].

See other REDOX REACTIONS

Ammonium nitrate

Mellor, 1923, Vol. III, 284

Evaporation of mixed solutions gives violent decomposition during concentration.

Hydrazine, Ethanol

Hofmann, K. A. *et al., Annalen*, 1899, **305**, 222

A blue crystalline complex, assigned a monohydrazino structure, was obtained from the nitrate and hydrazine hydrate in ethanol. It exploded on heating or, sometimes, after thorough drying in a desiccator, on shaking.

See also AMMINEMETAL NITRATES

1-Hydroxybenzotriazole, Ethanol

Anon., *Safety Digest Univ. Safety Assoc.*, 1992, **44**, 24

A mixture of the above was evaporated to dryness, on scraping the residue with a spatula a 'dust explosion', presumably of only a small part of the charge, resulted, covering the experimenter with powder.

See 1-Hydroxybenzotriazole

See 1-Hydroxybenzotriazole

See also AMMINEMETAL NITRATES

See other REDOX REACTIONS

Organometallic materials

Buffinger, D. R., *et al., J. Coord. Chem.*, 1988, **19**(1-3), 197

A double salt of the nitrate and the copper(II) salt of an organometallic ligand was found to explode at around 100°C. In view of the oxidising powers of the nitrate, complexes of this nature are not likely to be stable.

See ORGANOMETALLIC NITRATES

Other reactants

Yoshida, 1980, 198

MRH values calculated for 19 combinations with oxidisable materials are given.

Potassium hexacyanoferrate(II)

Wolski, J. *et al., Explosivstoffe*, 1969, **17**(5), 103—110

Interaction is explosive at 220°C.

Tin MRH 2.68/62

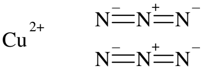
Ellern, 1968, 46

Tin foil in contact with a solution of the nitrate may ignite or give sparks.

See other METAL NITRATES

4274. Copper(II) azide

[14215-30-6] **CuN_6**



$Cu^{2+}\quad \overset{-}{N}{=}\overset{+}{N}{=}N^{-}\quad \overset{-}{N}{=}\overset{+}{N}{=}N^{-}$

1. Mellor, 1940, Vol. 8, 348; 1967, Vol. 8, Suppl. 2.2, 42—50
2. Urbanski, 1967, Vol. 3, 185
3. Jenkins, C. L. *et al., J, Org. Chem.*, 1971, **36**, 3095—3102
4. Sood, R. K. *et al., Chem. Abs*, 1997, **126**, 48910

The azide is very explosive, even when moist. Loosening the solid from filter paper caused frictional initiation. Explosion initiated by impact is very violent, and spontaneous explosion has also been recorded [1]. It is also an exceptionally powerful initiator [2]. Detonation of the azide when dry has been confirmed [3]. Good crystals are considerably more sensitive to shock, friction and electric discharge than is powder [4].

See Sodium azide: Heavy metals

See other METAL AZIDES

4275. Copper(II) oxide

[1317-38-0] **CuO**

$Cu{=}O$

Aluminium MRH 3.89/18

1. Krah, W., *Chem Abs.*, 1978, **89**, 89652
2. Haws. L. D. *et al., Chem. Abs.*, 1979, **90**, 189294

In demonstrating the use of powdered aluminium to reduce the oxide in a thermite-type reaction, the mixture must be heated behind a safety screen because of the small explosion produced [1]. Consolidation of the thermite mixture into a high-density composite gives chemical heat sources which are safe to handle [2].

See Metals, below

See other THERMITE REACTIONS

Anilinium perchlorate

See Anilinium perchlorate: Metal oxides

Barium acetate, Yttrium oxide

See Barium acetate: Copper(II) oxide, etc.

Boron
Mellor, 1946, Vol. 5, 17
The exothermic reaction on heating a mixture melted the glass container.
See other GLASS INCIDENTS

Dichloromethylsilane
See Dichloromethylsilane: Oxidants

Hydrogen
Read, C. W. W., *School Sci. Rev.*, 1941, **22**(87), 340
Reduction of the heated oxide in a combustion tube by passage of hydrogen caused a violent explosion. (The hydrogen may have been contaminated with air.)

Hydrogen sulfide MRH 0.59/30
See Hydrogen sulfide: Metal oxides
Hydrogen trisulfide: Metal oxides

Metals MRH values below show % of metal
1. Browne, T. E., *School Sci. Rev.*, 1967, **48**(166), 921
2. Vella, A. J., *J. Chem. Educ.* 1994, **71**(4), 328

An attempted thermite reaction with aluminium powder and copper(II) oxide in place of iron(III) oxide caused a violent explosion. An anonymous comment suggests that a greater reaction rate and exothermic effect were involved, and adds that attempted use of silver oxide would be even more violent [1]. An explosion resulted from heating a mixture of copper(II) oxide and magnesium in a school laboratory. Avoidance of magnesium thermites in teaching is counselled [2].
See Aluminium, above
Aluminium: Metal oxides MRH 3.89/18
Magnesium: Metal oxides MRH 4.30/23
Potassium: Metal oxides
Sodium: Metal oxides MRH 2.05/37

Other reactants
Yoshida, 1980, 127
MRH values calculated for 7 combinations, largely with oxidisable materials, are given.

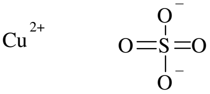
Phospham
See Phospham: Oxidants

Phthalic anhydride
'Leaflet No. 5', Inst. of Chem., London, 1940
A mixture of the anhydride and anhydrous oxide exploded violently on heating.

Reducants MRH Hydrazine 1.17/17
Mellor, 1941, Vol. 3, 137
Interaction with hydroxylamine or hydrazine is vigorous.
See other METAL OXIDES

Rubidium acetylide
See Rubidium acetylide: Metal oxides

4276. Copper(II) sulfate
[18939-61-2] **CuO_4S**



HCS 1980, 327

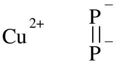
Hydroxylamine
See Hydroxylamine: Copper(II) sulfate
See other METAL OXONON-METALLATES

4277. Copper monophosphide
[12517-41-8] **CuP**

Cu^{3+} P^{3-}

See Copper(II) phosphide
See other METAL NON-METALLIDES

4278. Copper diphosphide
[12019-11-3] **CuP_2**



See Copper(II) phosphide
See other METAL NON-METALLIDES

4279. Copper(II) sulfide
[1317-40-4] **CuS**

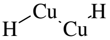
$Cu\equiv S$

Chlorates
Mellor, 1956, Vol. 2, Suppl. 1, 584
Copper(II) sulfide explodes in contact with magnesium chlorate, zinc chlorate or cadmium chlorate, or with a conc. solution of chloric acid.
See METAL HALOGENATES

Other reactants
Yoshida, 1980, 391
MRH values calculated for 12 combinations with various reagents are given.
See other METAL SULFIDES

4280. Copper(I) hydride

[13517-00-5] **Cu_2H_2**



Gibson, 1969, 77

The dry hydride ignites in air.

Halogens

Mellor, 1941, Vol. 3, 73

Ignition occurs on contact with fluorine, bromine or iodine.

See other METAL HYDRIDES

4281. Copper(I) azide

[14336-80-2] **Cu_2N_6**

$$N^{-}{=}N^{+}{=}N^{-} \quad Cu^{+}{-}Cu^{+} \quad N^{-}{=}N^{+}{=}N^{-}$$

1. Mellor, 1940, Vol. 8, 348; 1967, Vol. 8, Suppl. 2.2, 42—50
2. Urbanski, 1967, Vol. 3, 185

It is highly endothermic (ΔH_f° (s) 253.1 kJ/mol, 2.40 kJ/g). One of the more explosive metal azides, it decomposes at 205°C [1], and is very highly impact-sensitive [2].

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

4282. Copper(I) oxide

[1317-39-1] **Cu_2O**

$$Cu^{+} \quad Cu^{+} \quad O^{2-}$$

Aluminium

Moddeman, W. E. *et al., Chem. Abs.*, 1981, **84**, 159186

The role of surface chemistry in reactivity of this thermite combination has been studied.

See other THERMITE REACTIONS

Lithium nitride

See Lithium nitride: Copper(I) chloride, etc.

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

See other METAL OXIDES

4283. Copper(I) nitride

[1308-80-1] **Cu_3N**

$$Cu^{+} \quad Cu^{+} \quad Cu^{+} \quad N^{3-}$$

Mellor, 1940, Vol. 8, 100

It is mildly endothermic (ΔH_f° (s) +74.5 kJ/mol, 0.36 kJ/g). It may explode on heating in air.

Nitric acid

See Nitric acid: Copper(I) nitride

See other N-METAL DERIVATIVES

4284. Copper(II) phosphide

[12134-35-9] $\mathbf{Cu_3P_2}$

$$Cu^{2+} \quad Cu^{2+} \quad Cu^{2+} \quad P^{3-} \quad P^{3-}$$

Oxidants

Mellor, 1940, Vol. 8, 839

The powdered phosphide burns vigorously in chlorine. Mixtures with potassium chlorate explode on impact, and with potassium nitrate, on heating. The monophosphide and diphosphide behave similarly.

See Potassium chlorate: Metal phosphides

See other METAL NON-METALLIDES

†4285. Deuterium oxide

[7789-20-0] $\mathbf{D_2O}$

$$\mathbf{D_2O}$$

1. Anderson, C., *Nature*, 1992, **355**(6356), 102
2. Baum, R., *Chem. Eng. News,* 1992, **70**(26), 8
3. Zhang, X. *et al., Front. Sci. Ser.*, 1993, (4[Frontiers of Cold Fusion]), 381

Electrolysis of heavy water over palladium electrodes is claimed to give inexplicable energy release – ‘Cold Fusion’. It can certainly kill [1], even though the mechanism be ignition of an explosive mixture of deuterium and oxygen resulting from past electrolysis after a platinum recombination catalyst for the off-gases failed and a safety valve blocked. The cell then exploded when the experimenter picked it up; ignition presumably at a catalytic surface exposed by moving liquid [2]. Others hold out for less probable causes [3].

Pentafluorophenyllithium

See Diprotium monoxide

See Pentafluorophenyllithium: Deuterium oxide

See other NON-METAL OXIDES

4286. Europium

[7440-53-1] **Eu**

Eu

Bailar, 1973, Vol. 4, 69

Europium is the most reactive lanthanide metal, and may ignite on exposure to air if finely divided.
See LANTHANIDE METALS: OXIDANTS
See other METALS, PYROPHORIC METALS

4287. Europium(II) sulfide

[12020-65-4] **EuS**

$$\mathrm{Eu{=}S}$$

Sidgwick, 1950, 454
Pyrophoric in air.
See other METAL SULFIDES, PYROPHORIC MATERIALS

4288. Hydrogen fluoride

[7664-39-3] **FH**

$$\mathrm{H{-}F}$$

(*MCA SD-25*, 1970); Soln. *NSC 459*, 1978; *HCS 1980*, 543; Gas *HCS 1980*, 548

1. Keen, M. J. *et al., Chem. & Ind.*, 1957, 805
2. Braker, 1980, 391
3. Anon., *Lab. Hazards Bull.*, 1991, **11**(09), 556
4. Watson, E. F., *Chem. Eng. News*, 1997, **75**(17), 28, 6

Handling precautions for the gas or anhydrous liquid are detailed [1], and a polythene condenser for disposal of hydrogen fluoride is described [2]. A steel cylinder of the nominally anhydrous material exploded after 42 years. This is attributed to ppm levels of water, which catalyses reaction with the steel to produce hydrogen, slowly increasing the pressure. It is recommended that cylinders should be vented at yearly intervals, and those more than two years old returned to the manufacturer [3]. More warnings against prolonged storage in steel are given [4].

Bismuthic acid
See Bismuthic acid: Hydrofluoric acid

Cyanogen fluoride
See Cyanogen fluoride: Hydrogen fluoride

Glycerol, Nitric acid
See Nitric acid: Glycerol, etc.

Mercury(II) oxide, Organic materials
Ormston, J., *School Sci. Rev.*, 1944, **26**(98), 32
During the fluorination of organic materials by passing hydrogen fluoride into a vigorously stirred suspension of the oxide (to form transiently mercury difluoride, a powerful fluorinator), it is essential to use adequate and effective cooling below 0°C to prevent loss of control of the reaction system.

Metal alloys
  Young, J. A., *Chem. Health and Safety*, 1995, **2**(2), 6
  It is reported that an aluminium cleaner containing low concentrations of hydrofluoric acid can generate stibine from antimony containing bearing-metal alloys, to the permanent detriment of the health of nearby workers. Presumably arsine could appear from arsenic containing alloys; both are gases and extremely toxic.

Methanesulfonic acid
  Gramstad, T. *et al., J. Chem., Soc.*, 1956, 173—180
  Electrolysis of a mixture produced oxygen difluoride which exploded.
  See Oxygen difluoride

Nitric acid, Lactic acid
  See Nitric acid: Hydrofluoric acid, Lactic acid

Nitric acid, Propylene glycol
  See Nitric acid: Hydrofluoric acid, Propylene glycol

Other reactants
  Yoshida, 1980, 311
  MRH values calculated for 7 combinations with various reagents are given.

Oxides MRH Calcium oxide 2.84/59
  Mellor, 1956, Vol. 2, Suppl. 1, 122; 1939, Vol. 9. 101
  Arsenic trioxide and calcium oxide incandesce in contact with liquid hydrogen fluoride.

N-Phenylazopiperidine
  See *N*-Phenylazopiperidine: Hydrofluoric acid

Phosphorus(V) oxide
  See Tetraphosphorus decaoxide: Hydrogen fluoride

Potassium permanganate
  See Potassium permanganate: Hydrofluoric acid

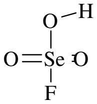
Potassium tetrafluorosilicate(2—)
  Mellor, 1956, Vol. 2, Suppl. 1, 121
  Contact with liquid hydrogen fluoride causes violent evolution of silicon tetrafluoride. (The same is probably true of metal silicides and other silicon compounds generally.)
  See Dialuminium octavanadium tridecasilicide

Sodium MRH 6.94/53
  See Sodium: Acids

Sulfuric acid
  See Sulfuric acid: Hydrofluoric acid
  See other INORGANIC ACIDS, NON-METAL HALIDES, NON-METAL HYDRIDES

4289. Fluoroselenic acid

[14986-53-9] **FHO_3Se**



Cellulose

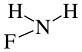
Bartels, H. *et al., Helv. Chim. Acta*, 1962, **45**, 179

A strong oxidant which reacts violently with filter paper or similar organic matter, igniting it if dry.

See other INORGANIC ACIDS, OXIDANTS

4290. Fluoramine (Fluoramide)

[15861-05-9] **FH_2N**



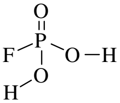
1. Hoffmann, C. J., *et al., Chem. Rev.*, 1962, **62**, 7
2. Minkwitz, R. *et al., Z. Naturforsch. B, Chem. Sci.*, 1988, **43B**, 1478—1480

The impure material is very explosive [1]. The pure material, prepared by a thermolytic method ,is stable as a solid at —103°C, but on melting it decomposes to ammonium hydrogen difluoride and nitrogen [2].

See other N-HALOGEN COMPOUNDS

4291. Fluorophosphoric acid

[13537-32-1] **FH_2O_3P**



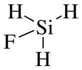
Sodium tetrahydroborate

See Sodium tetrahydroborate: Acids

See other INORGANIC ACIDS

4292. Fluorosilane

[13537-33-2] **FH_3Si**



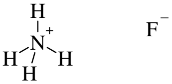
Azidogermane

See Azidogermane: Fluorosilane

See other HALOSILANES

4293. Ammonium fluoride

[16099-75-5] **FH_4N**



Chlorine trifluoride

See Chlorine trifluoride: Ammonium fluoride

See related METAL HALIDES

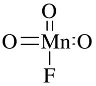
4294. Potassium fluoride hydrogen peroxidate

[32175-44-3] **$FK.H_2O_2$**

See entry CRYSTALLINE HYDROGEN PEROXIDATES

4295. Manganese fluoride trioxide

[22143-20-0] **$FMnO_3$**



Alone, or Organic compounds, or Water

Engelbrecht, A. *et al., J. Amer. Chem. Soc.*, 1954, **76**, 2042—2044

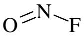
It decomposes, usually explosively, above 0°C or in contact with moisture. It is a powerful oxidant and reacts violently with organic compounds.

See other OXIDANTS

See related METAL HALIDES, METAL OXIDES

4296. Nitrosyl fluoride

[7789-25-5] **FNO**



Haloalkene (unspecified)

MCA Case History No. 928

Interaction of a mixture in a pressure vessel at —78°C caused it to rupture when moved from the cooling bath.

Metals, or Non-metals

1. Schmutzler, R., *Angew. Chem. (Intern. Ed.)*, 1968, **7**, 442
2. Pascal, 1956, Vol. 10, 346

Antimony, bismuth, arsenic, boron, red phosphorus, silicon [1] and tin [2] all react with incandescence.

Oxygen difluoride

Ruff, O. *et al., Z. Anorg. Chem.*, 1932, **208**, 293

Explosion occurs on mixing, even at low temperatures.

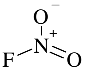
Sodium

Mellor, 1940, Vol. 8, 612

Reaction is incandescent.

See other N-HALOGEN COMPOUNDS, NON-METAL HALIDES, OXIDANTS

4297. Nitryl fluoride
[10022-50-1] **FNO_2**



Metals

Aynsley, E. E. *et al., J. Chem. Soc.*, 1954, 1122

When nitryl fluoride is passed at ambient temperature over molybdenum, potassium, sodium, thorium, uranium or zirconium, glowing or white incandescence occurs. Mild warming is needed to initiate similar reactions of aluminium, cadmium, cobalt, iron, nickel, titanium, tungsten, vanadium or zinc, and 200—300°C for lithium or manganese.

Non-metals

Aynsley, E. E. *et al., J. Chem. Soc.*, 1954, 1122

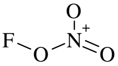
Boron and red phosphorus glow in the fluoride at ambient temperature, while hydrogen explodes at 200—300°C. Carbon and sulfur are also attacked.

Sodium azide

See Sodium azode: Nitryl fluoride

See other N-HALOGEN COMPOUNDS, NON-METAL HALIDES, OXIDANTS

4298. Nitryl hypofluorite ('Fluorine nitrate')
[7789-26-6] **FNO_3**



1. Schmutzler, R., *Angew. Chem. (Intern. Ed.)*, 1968, **7**, 454
2. Engelbrecht, A., *Monatsh.*, 1964, **95**, 633
3. Lustig, M. *et al., Adv. Fluorine Chem.*, 1973, 7, 189
4. Christe, K. O. *et al., Inorg. Chem.*, 1987, **56**, 920

It is mildly endothermic (ΔH_f° (g) $+10.4$ kJ/mol, 0.12 kJ/g) but a powerful oxidant.

It is a toxic colourless gas which is dangerously explosive in the gaseous, liquid and solid states [1]. It is produced during electrolysis of nitrogenous compounds in hydrogen fluoride [2]. Later work (perhaps with purer material?) did not show the explosive instability [3]. The shock-sensitivity is confirmed [4].

Gases

Hoffmann, C. J., *Chem. Rev.*, 1964, **64**, 94

Immediate ignition in the gas phase occurs with ammonia, dinitrogen oxide or hydrogen sulfide.

Organic materials

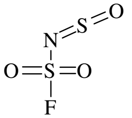
Brauer, 1963, 189

The very powerful liquid oxidant explodes when vigorously shaken, or immediately on contact with alcohol, ether, aniline or grease. It is also sensitive in the vapour or solid state (but see reference 3 above).

See Nitryl hypochlorite

See other ENDOTHERMIC COMPOUNDS, OXIDANTS

4299. Sulfur oxide-(*N*-fluorosulfonyl)imide (Sulfinylsulfamoyl fluoride)
[16829-30-4] **FNO_3S_2**



Water

Roesky, H. W., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 711

It reacts explosively with water at ambient temperature, but smoothly at —20°C.

See other ACYL HALIDES, N—S COMPOUNDS

4300. Thiazyl fluoride
[18820-63-8] **FNS**

$F{-}S{\equiv}N$

Alkylbutadienes

Bludssus, W. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 35—36

Interaction with, for example, 2,3-dimethylbutadiene is explosive.

See other NON-METAL HALIDES, N—S COMPOUNDS

4301. Fluorine azide
[14986-60-8] **FN_3**

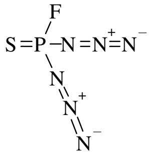
$\overset{-}{N}{=}\overset{+}{N}{=}N{-}F$

1. Bauer, S. H., *J. Amer. Chem. Soc.*, 1947, **69**, 3104
2. Gholivand, K. *et al., Inorg. Chem.*, 1987, **26**, 2137—2140

This unstable material usually explodes on vaporisation (at —82°C) [1]. It is extremely explosive in the liquid and solid states. A safe method has been developed for preparing the pure gas on 20 mg scale. It may be stored safely at 10—20 mbar/ —80°C for several months. Cooling the gas to —196°C, or evaporation of the liquid

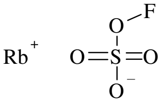
at a fast rate may lead to very violent explosions. Fluorine azide is now described as triazadienyl fluoride [2], as shown above.
See other HALOGEN AZIDES

4302. Fluorothiophosphoryl diazide
[38005-27-5] **FN_6PS**



O'Neill, S. R. *et al., Inorg. Chem.*, 1972, **11**, 1630
The explosion of the glassy material at —183°C was attributed to crystallisation of the glass.
See other ACYL AZIDES

4303. Rubidium fluoroxysulfate
[73347-64-5] (ion) **FO_4RbS**



Appelman, E. H. *et al., J. Amer. Chem. Soc.*, 1979, **101**, 388
This and the caesium analogue, both powerful oxidants, detonate mildly at 100°C, evolving oxygen.
See other ACYL HYPOHALITES, OXIDANTS

4304. Fluorine
[7782-41-4] **F_2**

F—F

FPA H79, 1979 (cylinder); *HCS 1980*, 503 (cylinder)

1. Kirk-Othmer, 1966, Vol. 9, 506
2. Gall, J. F. *et al., Ind. Eng. Chem.*, 1947, **39**, 262
3. Landau, R. *et al., Ind. Eng. Chem.*, 1947, **39**, 262
4. Turnbull, S. G. *et al., Ind. Eng. Chem.*, 1947, **39**, 286
5. Long, G., *Apparatus for Disposal of Fluorine on a Laboratory Scale*, Harwell, AERE, 1956
6. Gordon, J. *et al., Ind. Eng. Chem.*, 1960, **52**(5), 63A
7. Farrar, R. L. *et al., Some Considerations in the Handling of Fluorine and the Chlorine Fluorides*, Union Carbide Oak Ridge Rept. K/ET-252 for US DoE, 1979

8. Ring, R. J. *et al., Review of Fluorine Cells and Production*, Lucas Heights, Aus. At. En. Comm., 1973
9. Bailar, 1973, Vol. 2, 1015—1019
10. O'Hare, P., *NATO Sci. Ser., Ser. C*, 1999, **535**, 55
11. DesMarteau, D. D. *et al., J. Amer. Chem. Soc.*, 1987, **109**, 7194—7196
12. Maya, F. *et al., Tetrahedron*, 2004, **60**(1), 81

Fluorine is the most electronegative and reactive element known, reacting, often violently, with most of the other elements and their compounds (note the large MRH values quoted below). Handling hazards and disposal of fluorine on a laboratory scale are adequately described [1,2,3,4,5,6], and a more general review is also available [7]. Although once considered uncontrollable as a fluorinating agent in organic synthesis, increasing success has been obtained with diluted fluorine: helium, with which it does not react, is the best diluent. It is recommended that synthetic chemists do not try to make dilute mixtures themselves [12]. Safety practices associated with the use of laboratory- and industrial-scale fluorine cells and facilities have been reviewed [8]. Equipment and procedures for the laboratory use of fluorine and volatile fluorides have been detailed [9] including fluorine bomb calorimetry [10]. A new series of *N*-fluorosulfonimides shows promise as milder and safer reagents than elemental fluorine for aromatic fluorination [11].

Acetonitrile, Chlorine fluoride

Sekiya, A. *et al., Inorg. Chem.*, 1981, **20**, 1—2

When fluorine was condensed onto acetonitrile and chlorine fluoride frozen at —196°C, a small explosion occurred in the reactor.

Acetylene MRH 11.92/41

See Acetylene: Halogens

Alkanes, Oxygen

Von Elbe, G., US Pat. 3 957 883, 1976

Interaction of propane, butane or 2-methylpropane with fluorine and oxygen produces peroxides. Appropriate reaction conditions are necessary to prevent explosions.

Ammonia MRH 10.25/23

1. Mellor, 1940, Vol. 8, 216
2. Müller, W., *Umsch. Wiss. Tech.*, 1974, **74**(15), 485—486

Ammonia ignites in contact with fluorine [1], and the anhydrous liquids have been used as a propellant pair [2]. Aqueous ammonia ignites or explodes on contact [1].

See Water, below

Boron nitride

Moissan, 1900, 232

Unheated interaction leads to incandescence.

Caesium fluoride, Fluorocarboxylic acids

Sekiya, A. *et al., Inorg. Chem.*, 1980, **19**, 1329

Low temperature fluorination of fluorocarboxylic acids to give explosive 1,1-bis(-fluoroxy)perfluoroalkanes occasionally led to explosive reactions. Thus difluoroacetic acid led to explosion at —195°, and perfluorosuccinic acid at —111° or —20°C.

See BIS(FLUOROOXY)PERHALOALKANES

Caesium heptafluoropropoxide

1. Gumprecht, W. H., *Chem. Eng. News*, 1965, **43**(9), 36
2. *MCA Case History No. 1045*

Fluorination of caesium heptafluoropropoxide at —40°C with nitrogen-diluted fluorine exploded violently after 10 h. This may have been caused by ingress of moisture, formation of some pentafluoropropionyl derivative and conversion of this to pentafluoropropionyl hypofluorite, known to be explosive if suitably initiated. Other possible explosive intermediates are peroxides or peresters.

See Pentafluoropropionyl hypofluorite

Ceramic materials

Farrar, R. L. *et al., US DoE Rept. K/ET-252*, 1979, 9

Even finely divided ceramic materials may be ignited in fluorine.

Covalent halides

1. Mellor, 1940, Vol. 2, 12; 1956, Vol. 2, Suppl. 1, 64; 1940, Vol. 8, 995, 1003, 1013
2. Leleu, *Cahiers*, 1973, (73), 509; 1974, (74), 427

Chromyl chloride at high concentration ignites in fluorine, while phosphorus pentachloride, phosphorus trichloride and phosphorus trifluoride ignite on contact [1]. Boron trichloride ignites in cold fluorine, and silicon tetrachloride on warming [2].

Cyanogen (Dicyanogen)

Klapötke, T. M. *et al., Angew. Chemie (Int.)*, 1991, **30**(11), 1485

An explosion was experienced on allowing a mix of these reagents, with arsenic pentafluoride, which had been uv irradiated at —196°C, to warm to —85°C.

See Halogens, below

Cyanoguanidine

Rausch, D. A. *et al., J. Org. Chem.*, 1968, **33**, 2522

The products, perfluoro-1-aminomethylguanidine and perfluoro-*N*-aminomethyltriaminomethane, and by-products of the reaction of fluorine with cyanoguanidine are extremely explosive in gas, liquid and solid states.

See Sodium dicyanamide, below

Graphite

1. Lagow, R. J. *et al., J. Chem. Soc., Dalton Trans.*, 1974, 1270
2. Ruff, O. *et al., Z. Anorg. Chem.*, 1934, **217**, 1
3. Simons, J. H. *et al., J. Amer. Chem. Soc.*, 1939, **61**, 2962—2966
4. Farrar, R. L. *et al., US DoE Rpt. K/ET-252*, 1979, 33—34
5. Kita, Y. *et al., Chem. Abs.*, 1983, **99**, 107531

During interaction at ambient temperature in a bomb to produce poly(carbon monofluoride), admission of fluorine beyond a pressure of 13.6 bar must be extremely slow and carefully controlled to avoid a violently exothermic explosion [1]. Previously it had been shown that explosive interaction of carbon and fluorine was due to the formation and decomposition of the graphite intercalation compound, poly(carbon monofluoride)

[2]. Presence of mercury compounds prevents explosion during interaction of charcoal and fluorine [3]. Reaction of surplus fluorine with graphite or carbon pellets was formerly used as a disposal method, but is no longer recommended. Violent reactions observed when an exhausted trap was opened usually involved external impact on the metal trap, prodding the trap contents to empty the trap, or possibly ingress of moist air [4]. Removal of higher fluorocarbons (above C_4) from the circulating gas stream prevents explosive decomposition of the graphite fluoride [5].

Halocarbons MRH Carbon tetrachloride 2.34/67, chloroform 3.77/56

1. Mellor, 1956, Vol. 2, Suppl. 1, 198
2. Schmidt, 1967, 82
3. Fletcher, E. A. *et al., Combust. Inst. Paper WSS/CI-67-23*, 1967
4. Moissan, 1900, 241
5. Farrar, R. L. *et al., US DoE Rept. K/ET-252*, 1979, 36—40

The violent or explosive reactions which carbon tetrachloride, chloroform, etc., exhibit on direct local contact with gaseous fluorine [1], can be moderated by suitable dilution, catalysis and diffused contact [2]. Combustion of perfluorocyclobutane—fluorine mixtures was detonative between 9.04 and 57.9 vol% of the halocarbon [3]. Iodoform reacts very violently with fluorine owing to its high iodine content [4]. Explosive properties of mixtures with 1,2-dichlorotetrafluoroethane have been studied [5].

See Poly(tetrafluoroethylene), etc., below

Halogens, or Dicyanogen MRH values below references

1. Mellor, 1940, Vol. 2, 12
2. Sidgwick, 1950, 1148
3. Tari, I. *et al., Inorg. Chem.*, 1979, **18**, 3205

MRH Bromine 1.38/89, chlorine 1.67/38, iodine 3.89/43

While bromine, iodine and dicyanogen all ignite in fluorine at ambient temperature [1], a mixture of chlorine and fluorine (containing essential moisture) needs sparking before ignition occurs, though an explosion immediately follows [2]. Heating fluorine and chlorine in a Monel pressure vessel gives contained explosions at around 100°C [3].

See Cyanogen, above

Hexalithium disilicide

Mellor, 1940, Vol. 6, 169

It incandesces on warming in fluorine.

Hydrocarbons MRH Anthracene 7.57/49, acetylene 11.92/41

1. Mellor, 1940, Vol. 2, 11; 1956, Vol. 2, Suppl.1, 198
2. Sidgwick, 1950, 1117
3. Schmidt, 1967, 82
4. Moissan, 1900, 240—241

Violent explosions occur when fluorine directly contacts liquid hydrocarbons, even at —210 with anthracene or turpentine, or solid methane at —190°C with liquid fluorine. Many lubricants ignite in fluorine [1,2]. Contact and reaction under carefully controlled conditions with catalysis can now be effected smoothly [3]. Gaseous hydrocarbons (town gas, methane) ignite in contact with fluorine, and mixtures with unsaturated hydrocarbons (ethylene, acetylene) may explode on exposure to sunlight. Each bubble of fluorine passed through benzene causes ignition, but a rapid stream may lead to explosion [4].

Hydrofluoric acid

See Hydrogen halides, below

Hydrogen MRH 13.39/5

1. Mellor, 1940, Vol. 2, 11; 1956, Vol. 2, Suppl.1, 55
2. Sidgwick, 1950, 1102
3. Kirshenbaum, 1956, 46
4. Gmelin, 1980, Fluorine, Suppl. Vol. 2
5. Truby, F. K., *J. Appl. Phys.*, 1978, **49**, 3481—3484

The violently explosive reactions which sometimes occur when the 2 elements come into contact under conditions ranging from solid fluorine and liquid hydrogen at —252°C to the mixed gases at ambient temperature [1] are caused by the catalytic effects of impurities or the physical nature of the walls of the containing vessel [2]. Even in absence of such impurities, spontaneous explosions still occur in the range of 75—90 mol% fluorine in the gas phase [3]. Data, including the inhibiting effect of small amounts of oxygen, has been reviewed [4], but presence of relatively large amounts does not necessarily inhibit explosions [5].

Hydrogen fluoride, Seleninyl fluoride

Seppelt, K., *Angew. Chem. (Intern. Ed.)*, 1972, **11**, 630

Preparation of pentafluoroorthoselenic acid from the above reagents in an autoclave above ambient temperature caused occasional explosions. A safer alternative preparation is described.

Hydrogen halides MRH HBr 2.30/8, HCl 3.18/65, HI 1.97/87

Mellor, 1940 Vol. 2, 12

Hydrogen bromide, hydrogen chloride and hydrogen iodide ignite in contact with fluorine, and the conc. aqueous solutions, including that of hydrogen fluoride, also produce flame.

Hydrogen sulfide

See Sulfides, below

Hydrogen, Oxygen

Getzinger, R. W., *Rept. LA-5659*, Los Alamos Sci. Lab., 1974

The conditions under which mixtures of the gases at 1 bar and ambient temperature will react non-explosively have been studied.

Ice

1. English, W. D. *et al., Cryog. Technol.*, 1965, **1**, 260
2. *UK Scientific Mission Report 68/79*, Washington, UKSM, 1968

Mixtures of liquid fluorine and ice are highly impact-sensitive, with a power comparable to that of TNT. Contact of moist air or water with liquid fluorine can thus be very hazardous [1,2].

See Water, below

Metal acetylides and carbides

Mellor, 1946, Vol. 5, 849, 885, 890—891

Monocaesium acetylide and caesium acetylide, lithium acetylide and rubidium acetylide, tungsten carbide and ditungsten carbide, and zirconium dicarbide all ignite in cold fluorine, while uranium dicarbide ignites in warm fluorine.

Metal borides

Bailar, 1973, Vol. 1, 729

Interaction frequently attains incandescence.

Metal cyanocomplexes

Moissan, 1900, 228

Potassium hexacyanoferrate(II), lead hexacyanoferrate(III) and potassium hexacyanoferrate(III) become incandescent in fluorine, and the liberated dicyanogen also ignites.

Metal hydrides

Mellor, 1940, Vol. 2, 12, 483; 1956, Vol. 2, Suppl. 1, 56; 1941, Vol. 3, 73

Copper hydride, potassium hydride and sodium hydride all ignite on contact with fluorine at ambient temperature.

Metal iodides

Moissan, 1900, 227

Fluorine decomposes calcium iodide, lead iodide, mercury iodide and potassium iodide at ambient temperature, and the liberated iodine ignites, evolving much heat.

Metal oxides MRH Calcium oxide 6.15/60

Mellor, 1940, Vol. 2, 13, 469; 1941, Vol. 3, 663; 1942, Vol. 13, 715; 1936, Vol. 15, 380, 399

Oxides of the alkali and alkaline earth metals and nickel(II) oxide incandesce in cold fluorine, and iron(II) oxide when warmed. Nickel(IV) oxide also burns in fluorine.

Metal salts MRH Potassium dichromate 2.97/66, potassium permanganate 3.18/67, sodium chlorate 2.34/85, sodium nitrate 1.34/56

1. Mellor, 1940, Vol. 2, 13; 1956, Vol. 2, Suppl. 1, 63
2. Schmidt, 1967, 83—84
3. Moissan, 1900, 228—239
4. Pascal, 1960, Vol. 16, 57—60
5. Fichter, F. *et al., Helv. Chim. Acta*, 1930, **13**, 99—102

Calcium carbonate, lead carbonate, basic lead carbonate and sodium carbonate all ignite and burn fiercely in contact with fluorine. Chlorides and cyanides are vigorously attacked by cold fluorine, including lead fluoride and thallium(I) chloride, both of which become molten. Mercury(II) cyanide ignites in fluorine when warmed gently, and silver cyanide reacts explosively when cold [1]. Sodium metasilicate ignites in fluorine [2]. Unheated calcium phosphate [3], sodium thiosulfate and sodium diphosphate [4] all incandesce in contact with fluorine, and barium thiocyanate or mercury thiocyanate ignites [3]. On warming, chromium(III) chloride [4], calcium arsenate or copper borate incandesce, and sodium arsenate ignites [3]. Introduction of fluorine into solutions of silver fluoride, silver nitrate, silver perchlorate or silver sulfate causes violent exothermic reactions to occur, with liberation of ozone-rich oxygen [5].

Metal silicides

Mellor, 1940, Vol. 6, 169, 178

Calcium disilicide readily ignites, and lithium hexasilicide becomes incandescent, when warmed in fluorine.

Metals

MRH Caesium 3.43/28, calcium 15.56/51, copper 3.01/76, lead 3.39/76, lithium 23.51/27, magnesium 17.78/39, manganese 8.91/49, molybdenum 7.57/46, potassium 9.58/68, rubidium 5.19/82, sodium 13.43/55, uranium 6.02/72, zinc 2.45/63

1. Mellor, 1940, Vol. 2, 13, 469; 1941, Vol. 3, 638; 1940, Vol. 4, 267, 476; 1946, Vol. 5, 421; 1939, Vol. 9, 379, 891; 1943, Vol. 11, 513, 730; 1942, Vol. 12, 344; 1942, Vol. 15, 675
2. Schmidt, 1967, 78—80
3. Kirk-Othmer, 1966, Vol. 9, 507—508

The vigour of reaction is greatly influenced by the state of sub-division of the metals involved. Massive calcium, moist magnesium, manganese powder, molybdenum powder, potassium, sodium, rubidium and antimony all ignite in cold fluorine gas. Warm tantalum powder or cold thallium ignites on contact with fluorine. Fine copper wire (as wool) ignites at 121°C, and osmium and tin begin to burn at 100°C, while iron powder (100-mesh, but not 20-mesh) ignites in liquid fluorine. Titanium will ignite if impacted under the liquid at —188°C and has ignited in presence of catalysts in the gas at —80°C, but in all cases the fluoride film prevents further propagation. Tungsten and uranium powders ignite in the gas without heating, while zinc ignites at about 100°C. Molybdenum, tungsten and Monel wires ignited in atmospheric fluorine at 205, 283 and 396°C (averaged values), respectively. Generally, strongly electropositive metals, or those forming volatile fluorides are attacked the most vigorously.

Miscellaneous materials

1. Mellor, 1940, Vol. 2, 13
2. Schmidt, 1967, 84, 110
3. Lafferty, R. H. *et al., Chem. Eng. News*, 1948,**26**, 3336

Town gas ignites in contact with gaseous fluorine, as does a mixture of lead oxide and glycerol (formerly used as a jointing compound) [1]. Spillage tests involving action of liquid fluorine alone or as a 30% solution in liquid oxygen caused asphalt and crushed limestone to ignite, and coke and charcoal to burn, the latter brilliantly, while JP4 liquid hydrocarbon fuel produced violent explosions and a large fireball. Humus-rich soil also burned with a bright flame [2]. Immersion of various glove materials in liquid fluorine was examined. Cotton exploded violently and Neoprene slightly with ignition, while leather charred but did not ignite [3].

Nitric acid MRH 0.50/53

1. Cady, G. H., *J. Amer. Chem. Soc.*, 1934, **56**, 2635
2. Schmutzler, R., *Angew. Chem. (Intern. Ed.)*, 1968, **8**, 453

Interaction of fluorine with either the concentrated or very dilute acid caused explosions, while use of 4N acid did not [1]. Later and safer methods of preparing nitryl hypofluorite are summarised [2].

Nitrogenous bases MRH Dimethylamine 10.63/23, pyridine 8.28/45

Hoffman, C. J., *Chem. Rev.*, 1962, **62**, 12

Aniline, dimethylamine and pyridine incandesce on contact with fluorine.

See Ammonia, and Cyanoguanidine, both above

Non-metal oxides MRH Carbon monoxide 6.44/42, dinitrogen tetraoxide 1.00/45, nitrogen oxide 2.93/99+, sulfur dioxide 5.10/36

1. Mellor, 1940, Vol. 2, 11; 1939, Vol. 9, 101
2. Hoffman, C. J. *et al., Chem. Rev.*, 1962, **62**, 10
3. Pascal, 1960, Vol. 16, 53, 62
4. Moissan, 1900, 138

Arsenic trioxide reacts violently and nitrogen oxide ignites in excess fluorine. Bubbles of sulfur dioxide explode separately on contacting fluorine, while addition of the latter to sulfur dioxide causes an explosion at a certain concentration [1]. Reaction of fluorine with dinitrogen tetraoxide usually causes ignition [2]. Interaction with carbon monoxide may be explosive. Anhydrous silica incandesces in the gas, and interaction with liquid fluorine at —80°C is explosive [3][4]. Boron trioxide also incandesces in the gas [3].

See Bis(fluoroformyl) peroxide

Non-metals MRH Arsenic 7.19/57, silicon 14.73/27, sulfur 8.28/22

1. Mellor, 1940, Vol. 2, 11, 12: 1956, Vol. 2, Suppl. 1, 60; 1946, Vol. 5, 785, 822; 1940, Vol. 6, 161; 1939, Vol. 9, 34; 1943, Vol. 11, 26
2. Schmidt, 1967, 52, 107
3. Pascal, 1960, Vol. 16, 58
4. Moissan, 1900, 125—128

Boron, phosphorus (yellow or red), selenium, tellurium and sulfur all ignite in contact with fluorine at ambient temperature, silicon attaining a temperature above 1400°C [1]. The reactivity shown by various forms of carbon (charcoal, lampblack, soot) all of which ignite and burn vigorously in fluorine [1] has been reported to be due to presence of various impurities, moisture and hydrocarbons [1,2]. Carefully purified carbon (massive graphite) is inert to fluorine at ambient or slightly elevated temperatures for a short period but may then react explosively [2]. Phosphorus [3] and sulfur incandesce in liquid fluorine, and sulfur ignites even at —188°C [4].

See Graphite, above

1- or 2-Fluoriminoperfluoropropane

Sekiya, A. *et al., J. Fluorine Chem.*, 1981, **17**, 463—468

Interaction is explosive.

Other reactants

Yoshida, 1980, 307—310

MRH values calculated for 58 combinations with a very wide variety of other reagents are given. Many of the values are extremely high.

Oxygenated organic compounds MRH Acetaldehyde 8.33/19, butanol 9.12/33, dimethylformamide 8.28/43, methanol 8.37/22

1. Pascal, 1960, Vol. 16, 65
2. Moissan, 1900, 242—245
3. Mellor, 1940, Vol. 2, 13

Methanol, ethanol and 3-methylbutanol [1], acetaldehyde, trichloroacetaldehyde [2] and acetone [3] all ignite in contact with gaseous fluorine. Lactic acid, benzoic acid and salicylic acid ignite, while gallic acid becomes incandescent. Ethyl acetate and methyl borate ignite in fluorine [2].

Perchloric acid

See Perchloric acid: Fluorine

Phosphorus halides

See Covalent halides, above

Polymeric materials, Oxygen

Schmidt, 1967, 87

Various polymeric materials were tested statically with both gaseous and liquefied mixtures of fluorine and oxygen containing from 50 to 100% of the former. The materials which burned or reacted violently were: phenol—formaldehyde resins (Bakelite); polyacrylonitrile—butadiene (Buna N); polyamides (Nylon); polychloroprene (Neoprene); polyethylene; polytrifluoropropylmethylsiloxane (LS63); polyvinyl chloride—vinyl acetate (Tygan); polyvinylidene fluoride—hexafluoropropylene (Viton); polyurethane foam. Under dynamic conditions of flow and pressure, the more resistant materials which burned were: chlorinated polyethylenes, polymethyl methacrylate (Perspex); polytetrafluoroethylene (Teflon).

Polytetrafluoroethylene

Appelman, E. H., *Inorg. Chem.*, 1969, **8**, 223

Teflon tubing, when used to conduct fluorine into a reaction mixture, sometimes ignites. Combustion stops when the flow of fluorine is shut off.

Polytetrafluoroethylene, Trichloroethylene

Lawler, A. E., *Advan. Cryog. Eng.*, 1967, **12**, 780—783

Tests showed that Teflon gaskets containing more than 0.35 wt% of sorbed trichloroethylene were potentially hazardous in contact with liquid fluorine.

See Halocarbons, above

Potassium chlorate

See Potassium chlorate: Fluorine

Potassium hydroxide

1. Fichter, F. *et al., Helv. Chim. Acta*, 1927, **10**, 551
2. Kacmarek, A. J. *et al., Inorg. Chem.*, 1962, **1**, 659—661
3. Bailar, 1973, Vol. 2, 789—791

Interaction at —20°C produces potassium trioxide, a spontaneously explosive solid [1]. Later references suggest that these compounds are not spontaneously explosive [2,3].

Purge gases

Farrar, R. L. *et al., US DoE Rept. K/ET-252*, 1979, 36

Purge gases used with liquid fluorine (—188°C or below) must be scrupulously dry and of low hydrocarbon content (<5 ppm), to prevent formation of ice crystals or solid hydrocarbons.

See Hydrocarbons, and Ice, both above

Sodium acetate MRH 6.44/35

Mellor, 1956, Vol. 2, Suppl. 1, 562

Application of fluorine to aqueous sodium acetate solution causes an explosion, involving formation of diacetyl peroxide.

See Diacetyl peroxide

Sodium bromate MRH 1.30/89

Appelman, E. H., *Inorg. Chem.*, 1969, **8**, 223

The oxidation of alkaline bromate by fluorine to perbromate is not smooth and small explosions may occur in the vapour above the solution. The reaction should not be run unattended.

Sodium dicyanamide

Rausch, D. A. *et al., J. Org. Chem.*, 1968, **33**, 2522

The product, perfluoro-*N*-cyanodiaminomethane, and many of the by-products from interaction of fluorine and sodium dicyanamide, are extremely explosive in gaseous, liquid and solid states.

See Cyanoguanidine, above

Stainless steel

Stewart, J. W., *Proc. 7th Int. Conf. Low Temp. Phys.*(Toronto), 1960, 671

During the study of phase transitions of solidified gases at high pressures, solid fluorine reacted explosively with apparatus made from stainless steel.

Sulfides MRH Antimony(III) sulfide 6.40/44, carbon disulfide 8.24/25, hydrogen sulfide 9.29/18

1. Mellor, 1940, Vol. 2, 11, 13; 1940, Vol. 6, 110; 1938, Vol. 9, 522; 1947, Vol. 10, 133; 1943, Vol. 11, 430
2. Moissan, 1900, 231—232

Antimony trisulfide, carbon disulfide vapour, chromium(II) sulfide and hydrogen sulfide all ignite in contact with fluorine at ambient temperature, the solids becoming incandescent [1]. Iron(II) sulfide reacts violently on mild warming, and barium sulfide, potassium sulfide or zinc sulfide all incandesce in the gas, as does molybdenum(III) sulfide at 200°C [2].

Trinitromethane

Smith, W. L. *et al., Chem. Abs.*, 1976, **84**, 46818

During preparation of fluorotrinitromethane, an instrumental method can be used to avoid occurrence of dangerous over-fluorination of nitroform.

Water

1. Mellor, 1940, Vol. 2, 11

2. Schmidt, 1967, 53, 119

Treatment of liquid air (containing condensed atmospheric moisture) with fluorine give a potentially explosive precipitate, thought to be fluorine hydrate [1]. Contact of liquid fluorine with a bulk of water causes violent explosions. Ice tends to react explosively with fluorine gas after an indeterminate induction period [2].

See other INDUCTION PERIOD INCIDENTS

Xenon, Catalysts

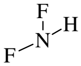
Levec, J. *et al., J. Inorg. Nucl. Chem.*, 1974, **36**, 997—1001

Interaction may be explosive in the presence of finely divided nickel fluoride or silver difluoride, or nickel(III) oxide or silver(I) oxide, or if initiated by local heating. The mechanism is discussed.

See other HALOGENS, OXIDANTS

4305. Difluoramine (Fluorimide)

[10405-27-3] **F_2HN**



1. Stevens, T. E., *J. Org. Chem.*, 1968, **33**, 2664, 2671
2. Petry, R. C. *et al., J. Org. Chem.*, 1967, **32**, 4034
3. Rosenfeld, D. D. *et al., J. Org. Chem.*, 1968, **33**, 2521
4. Martin, K. J., *J. Amer. Chem. Soc.*, 1965, **87**, 395
5. *MCA Case History No. 768*
6. Parker, C. O. *et al., Inorg. Synth.*, 1970, **12**, 310—311
7. Christe, K. O., *Inorg. Chem.*, 1975, **14**, 2821
8. Christe, K. O. *et al., Inorg. Chem.*, 1987, **26**, 920, 924
9. Chapman, R. D. *et al., J. Org. Chem.*, 1998, **63**(5), 1566

It is a dangerous explosive and must be handled with skill and care and appropriate precautions [1,2]. Explosions have occurred when it was condensed at —196°C [3] or allowed to melt [4], and a glass bulb containing the gas exploded violently when accidentally dropped [5]. Although difluoramine may be condensed safely at —78 or —130° [6], or at —142° [7], liquid nitrogen should not be used to give a trapping temperature of —196°C, as explosions are very likely to occur [6]. The solid adduct with caesium fluoride prepared at —142°C always explodes if allowed to warm towards 0°, and the adduct with rubidium fluoride sometimes exploded [8]. A safer procedure for handling difluoroamine is reported [9].

Benzenediazonium tetrafluoroborate, Caesium fluoride

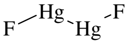
Baum, K., *J. Org. Chem.*, 1968, **33**, 4333

Use of caesium fluoride as base to effect condensation caused an explosion in absence of solvent. Pyridine or potassium fluoride, and use of dichloromethane gave satisfactory results.

See other N-HALOGEN COMPOUNDS

4306. Mercury(I) fluoride

[13967-25-4] **F_2Hg_2**



Iodoform

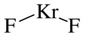
Andrews, L. *et al., J. Fluorine Chem.*, 1979, **13**, 273—278

Attempted fluorination of iodoform with a 10 year-old sample of mercury(I) fluoride led to an explosion immediately on heating.

See other MERCURY COMPOUNDS, METAL HALIDES

4307. Krypton difluoride

[13773-81-4] **F_2Kr**



ΔH_f° (g) 60 kJ/mol.

Ullmann, 1991, **A17**, 497

Krypton difluoride is a fluorinating agent some 50 kJ/mol more powerful than fluorine itself. It forms adducts, salts of FKr^+, with high valency fluorides such as AsF_5 and SbF_5, these react explosively with organic compounds.

Arsenic pentafluoride

Christe, K. O. *et al., Inorg. Chem.*, 1983, **22**, 3056

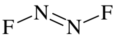
Interaction can lead to spontaneous exothermic decomposition of the fluoride accompanied by a bright flash and gas evolution. Safety precautions are required for this reaction system.

See other NON-METAL HALIDES (AND THEIR OXIDES)

See related XENON COMPOUNDS

4308. Difluorodiazene

[10578-16-2] **F_2N_2**



Bensoam, J. *et al., Tetrahedron Lett.*, 1977, 2797—2800

An explosion may occur when the diazene vapour is condensed, either to liquid or solid phases.

Both geometrical isomers are mildly endothermic (ΔH_f° (g) *cis*- +68.35 kJ/mol, 1.04 kJ/g; *trans*- +80.9 kJ/mol, 1.22kJ/g).

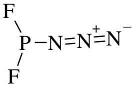
Hydrogen

Kuhn. L. P. *et al., Inorg. Chem.*, 1970, **9**, 60

Explosive interaction occurs above 90°C.

See other ENDOTHERMIC COMPOUNDS, N-HALOGEN COMPOUNDS

4309. Phosphorus azide difluoride
[37388-50-4] **F_2N_3P**

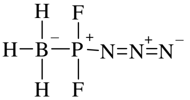


1. O'Neill. S. R. *et al., Inorg. Chem.*, 1972, **11**, 1630
2. Lines, E. L. *et al., Inorg. Chem.*, 1972, **11**, 2270

It is photolytically and thermally unstable and has exploded at 25°C. It is also explosively sensitive to sudden changes in pressure, as occur on expansion into a vacuum or in surging during boiling [1]. It also ignites in air [2].

See related HALOPHOSPHINES, NON-METAL AZIDES, NON-METAL HALIDES

4310. Phosphorus azide difluoride—borane
[38115-19-4] **$F_2N_3P.BH_3$**

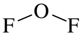


Lines, E. L. *et al., Inorg. Chem.*, 1972, **11**, 2270

The liquid complex exploded violently during transfer operations.

See related BORANES, NON-METAL AZIDES, NON-METAL HALIDES

4311. Oxygen difluoride
[7783-41-7] **F_2O**



It is mildly endothermic (ΔH_f° (g) +23.0 kJ/mol, 0.43 kJ/g).

Adsorbents

1. Metz, F. I., *Chem. Eng. News*, 1965, **43**(7), 41
2. Streng, A. G., *Chem. Eng. News*, 1965, **43**(12), 5
3. Streng, A. G., *Chem. Rev.*, 1963, **63**, 611

Mixtures of silica gel and the liquid difluoride sealed in tubes at 334 mbar exploded above —196°C, presence of moisture rendering the mixture shock-sensitive at this temperature [1]. Reaction of oxygen difluoride with silica, alumina, molecular sieve or similar surface-active solids is exothermic, and under appropriate conditions may be explosive [2]. A quartz fibre can be ignited in the difluoride [3].

See other MOLECULAR SIEVE INCIDENTS

Combustible gases

Streng. A. G., *Chem. Rev.*, 1963, **63**, 612

Mixtures with carbon monoxide, hydrogen and methane are stable at ambient temperatures, but explode violently on sparking. Hydrogen sulfide explodes with oxygen difluoride at ambient temperature and, though interaction is smooth at —78°C under reduced pressure, the white solid produced exploded violently when cooling was stopped.

Diborane

Rhein, R. A., *Combust. Inst. Paper WSC1-67-10*, 73—80, 1967

Although it reacts slowly at ambient temperature, a mixture of the components which is stable at —195°C could explode during warming to ambient conditions.

Diboron tetrafluoride

Holliday, A. K. *et al., J. Chem. Soc.*, 1964, 2732

Ignition occurred on mixing at, or on warming mixtures to, —80°C.

Halogens, or Metal halides

Streng, A. G., *Chem. Rev.*, 1963, **63**, 611

Mixtures with chlorine, bromine or iodine explode on warming. A mixture with chlorine passed through a copper tube at 300°C exploded with variable intensity. Aluminium chloride explodes in the difluoride, and antimony pentachloride lightly at 150°C.

Hexafluoropropene, Oxygen

Afonso, M. Dos Santos *et al., Chem. Abs.*, 1987, **107**, 175302

The thermal homogeneous chain reaction to give mainly octafluoropropane and hexafluoropropylene oxide becomes explosive above a minimum oxygen pressure of 26 mbar.

See other CATALYTIC IMPURITY INCIDENTS

Metals

Streng, A. G., *Chem. Rev.*, 1963, **63**, 611

Finely divided platinum group metals react on gentle warming, and coarser materials at higher temperatures; aluminium, barium, cadmium, magnesium, strontium, zinc and zirconium evolving light. Lithium, potassium and sodium incandesce brilliantly at 400°C, while tungsten explodes.

Nitrogen oxide

Streng, A. G., *Chem. Rev.*, 1963, **63**, 612

Gaseous mixtures may explode on sparking. The mixed gases slowly react to give a mixture (NO, NOF) which, if liquefied by cooling, will explode on warming.

Nitrosyl fluoride

Hoffman, C. J. *et al., Chem. Rev.*, 1962, **62**, 9

Solid mixture explodes on melting, and the gaseous components ignite on mixing.

Non-metals

1. Sidgwick, 1950, 1136
2. Streng, A. G., *Chem. Rev.*, 1963, **63**, 611

Pressure of the gas must be limited during concentration by contact with cooled charcoal to avoid violent explosions [1]. Red phosphorus ignites when gently warmed, and powdered boron and silicon generate sparks on heating in the difluoride [2].

Phosphorus(V) oxide

Streng, A. G., *Chem. Rev.*, 1963, **63**, 611

Ignition occurs spontaneously on contact.

Sulfur tetrafluoride

Oberhammer, H. *et al., Inorg. Chem.*, 1978, **17**, 1435

A mixture of the 2 fluorides, used at low temperature to prepare bis(pentafluorosulfur) oxide, is described as possibly explosive.

Water

Streng, A. G., *Chem. Rev.*, 1963, **63**, 610

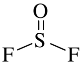
Presence of water or water vapour in oxygen difluoride is dangerous, the mixture (even when diluted with oxygen) exploding violently on spark ignition, especially at 100°C (i.e. with steam).

See Adsorbents, above

See other ENDOTHERMIC COMPOUNDS, HALOGEN OXIDES, OXIDANTS, OXYGEN FLUORIDES

4312. Sulfinyl fluoride

[7783-42-8] **F_2OS**



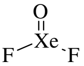
Sodium

See Sodium: Non-metal halides (reference 8)

See other NON-METAL HALIDES

4313. Xenon difluoride oxide

[13780-64-8] **F_2OXe**



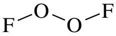
Alone, or Mercury, or Fluorides

1. Jacob, E. *et al., Angew. Chem. (Intern. Ed.)*, 1976, **15**, 158—159
2. Gillespie, R. J. *et al., J. Chem. Soc., Chem. Comm.*, 1977, 595—597

Although stable at below —40°C in absence of moisture, it will explode if warmed rapidly (> 20°C/h). Explosive decomposition of the solid difluoride oxide at —196°C occurs on contact with mercury, or antimony pentafluoride or arsenic pentafluoride [1]. The fluoride explodes at about 0°C, and also in contact with arsenic pentafluoride in absence of hydrogen fluoride at —78°C [2].

See other NON-METAL HALIDES, XENON COMPOUNDS

4314. Dioxygen difluoride
[7783-44-0] **F_2O_2**



It is mildly endothermic (ΔH_f° (g) +19.8 kJ/mol, 0.28 kJ/g) but a powerful oxidant.

Sulfur trioxide

Solomon, I. J. *et al., J. Chem. Eng. Data*, 1968, **13**, 530

Interaction of the endothermic fluoride with the trioxide is very vigorous, and explosive in absence of solvent.

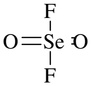
Various materials

Streng, A. G., *Chem. Rev.*, 1963, **63**, 615

Though not shock-sensitive, it is of limited thermal stability, decomposing below its b.p., —57°C, and explosively in contact with fluorided platinum at —113°C. It is a very powerful oxidant and reacts vigorously or violently with many materials at cryogenic temperatures. It explodes with methane at —194°, with ice at —140°, with solid ethanol at below —130° and with acetone—solid carbon dioxide at —78°C. Ignition or explosion may occur with chlorine, phosphorus trifluoride, sulfur tetrafluoride or tetrafluoroethylene, in the range —130 to —190°C. Even a 2% solution in hydrogen fluoride ignites solid benzene at —78°C.

See other ENDOTHERMIC COMPOUNDS, HALOGEN OXIDES, OXIDANTS, OXYGEN FLUORIDES

4315. Selenium difluoride dioxide
[14984-81-7] **F_2O_2Se**



$$\mathrm{O{=}\overset{F}{\underset{F}{Se}}{=}O}$$

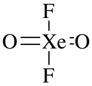
Ammonia

1. Bailar, 1973, Vol. 2, 966
2. Engelbrecht, A. *et al., Monatsh.*, 1962, **92**, 555, 581

Interaction is violent [1], and many of the products and derivatives are both shock- and heat-sensitive explosives [2]. These include the ammonium, potassium, silver and thallium salts of the 'triselenimidate' ion, systematically 2,4,6-tris(dioxoselena)perhydrotriazine-1,3-5-triide.

See other NON-METAL HALIDES

4316. Xenon difluoride dioxide
[13875-06-4] **F_2O_2Xe**

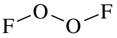


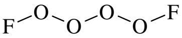
$$\mathrm{O{=}\overset{F}{\underset{F}{Xe}}{=}O}$$

Kirk Othmer, 1980, Vol. 12, 292
It is explosively unstable.

Preparative hazard
Xenon tetrafluoride oxide: Caesium nitrate
See Xenon hexafluoride: Water (reference 2)
See other XENON COMPOUNDS

4317. 'Trioxygen difluoride'
[16829-28-0] **F_2O_3**

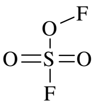




Bailar, 1973, Vol. 2, 761—763
This material is now considered to be an equimolar mixture of dioxygen difluoride and tetraoxygen difluoride, rather than the title species.

Various materials
Streng, A. G., *Chem. Rev.*, 1963, **63**, 619
Though thermally rather unstable, decomposing above its m.p., —190°C, it appears not to be inherently explosive. It is, however, an extremely potent oxidiser and contact with oxidisable materials causes ignition or explosions, even at —183°C. At this temperature, single drops added to solid hydrazine or liquid methane cause violent explosions, while solid ammonia, bromine, charcoal, iodine, red phosphorus and sulfur react with ignition and/or mild explosion. It is also extremely effective at initiating ignition of combustible materials in liquid oxygen, even at 0.1% concentration, whereas mixtures of ozone and fluorine in liquid oxygen are ineffective. This effect has been examined for use in hypergolic rocket propellant systems. Tetryl detonates spontaneously on contact with the difluoride.
See other HALOGEN OXIDES, OXIDANTS, OXYGEN FLUORIDES

4318. Fluorine fluorosulfate (Fluorosulfuryl hypofluorite)
[13536-85-1] **F_2O_3S**



1. Cady, G. H., *Chem. Eng. News*, 1966, **44**(8), 40
2. Cady, G. H. *et al., Inorg. Synth.*, 1968, **11**, 155
3. Cady, G. H., *Intra-Sci. Chem. Rep.*, 1971, **5**, 1
4. Lustig, M. *et al., Adv. Fluorine Chem.*, 1973, **7**, 175

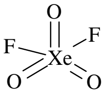
The crude fluorosulfate, produced as by-product in preparation of peroxodisulfuryl difluoride, was distilled into a cooled steel cylinder and, on warming to ambient temperature, the cylinder exploded. It decomposes at 200°C, but not explosively [1]. Preparative and handling procedures are detailed [2]. Further warnings on the need to handle with care have been given [3][4].

See other ACYL HYPOHALITES, OXIDANTS

See related ACYL HALIDES

4319. Difluorotrioxoxenon

[15192-14-0] **F_2O_3Xe**



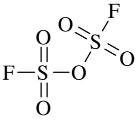
Kirk Othmer, 1980, **Vol. 12**, 292

Explosively unstable.

See other XENON COMPOUNDS

4320. Disulfuryl difluoride

[13036-75-4] **$F_2O_5S_2$**



Ethanol

Hayek, E., *Monatsh.*, 1951, **82**, 942

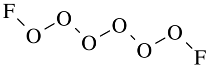
Violent reaction on mixing at ambient temperature.

See other ACYL HALIDES

See related ACID ANHYDRIDES

4321. Hexaoxygen difluoride

[12191-80-9] **F_2O_6**

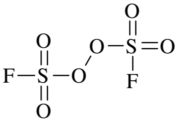


Bailar, 1973, Vol. 2, 764

Flashlight illumination or rapid warming of the solid at —213° to —183°C may lead to explosion.

See other HALOGEN OXIDES, IRRADIATION DECOMPOSITION INCIDENTS, OXYGEN FLUORIDES

4322. Peroxodisulfuryl difluoride (Bis(fluorosulfuryl)peroxide)
[13709-32-5] **$F_2O_6S_2$**



1. Shreeve, J. M. *et al., Inorg. Synth.*, 1963, **7**, 124
2. Zhang, D. *et al., J. Fluor. Chem.*, 1996, **76**(1), 83

A powerful oxidant which ignites organic materials on contact. Preparative and handling procedures are detailed [1,2].
See also INORGANIC PEROXIDES

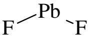
Boron nitride
See Tetra(boron nitride) fluorosulfate

Carbon monoxide
Gatti, R. *et al., Z. Phys. Chem.*, 1965, **47**, 323—336
Interaction proceeds explosively above 20°C.

Dichloromethane
Kirchmeier, R. L. *et al., Inorg. Chem.*, 1973, **12**, 2889
Equimolar amounts explode while warming together to ambient temperature after initial contact at —183°C. Dilution of the dichloromethane with trichlorofluoromethane prevented explosion at —20°C.
See Fluorine fluorosulfate

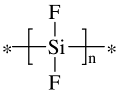
N-Fluoroiminosulfur tetrafluoride
See *N*-Fluoroiminosulfur tetrafluoride: Alone, etc.
See other ACYL HALIDES, DIACYL PEROXIDES, OXIDANTS

4323. Lead(II) fluoride
[7783-46-2] **F_2Pb**



Fluorine
See Fluorine: Metal salts
See other METAL HALIDES

4324. Poly(difluorosilylene)
[30582-57-1] **$(F_2Si)_n$**



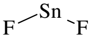
1. Bailar, 1973, Vol. 1, 1352
2. Perry, D. L. *et al., J. Chem. Educ.*, 1976, **53**, 696—699

Produced by condensation at low temperature, the rubbery polymer ignites in air [1], and preparation, handling and reactions have been detailed [2].

See other PYROPHORIC MATERIALS

See related HALOSILANES, NON-METAL HALIDES (AND THEIR OXIDES)

4325. Tin(II) fluoride
[7783-47-3] **F_2Sn**

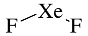


Magnesium nitrate

See Magnesium nitrate: Tin(II) fluoride

See other METAL HALIDES, REDUCANTS

4326. Xenon difluoride
[13709-36-9] **F_2Xe**



Shackelford, S. A., *J. Org. Chem.*, 1979, **44**, 3490—3492

Though a powerful oxidant, the difluoride is not explosively unstable. Safe procedures for the use of xenon difluoride in fluorination reactions are detailed. Residual traces of the fluoride are rapidly destroyed by dichloromethane at ambient temperatures.

Alkylaluminiums

Bulgakov, R. G., *et al., Chem. Abs.*, 1990, **112**, 7548

Reaction with diethoxyethylaluminium is explosive in the absence of solvent.

See ALKYLALUMINIUM ALKOXIDES AND HYDROXIDES, ALKYLMETALS

Combustible materials

Klimov, B. D. *et al., Chem. Abs.*, 1970, **72**, 85784

Xenon difluoride (or the tetrafluoride, or their mixtures) could not be caused to detonate by impact. Xenon difluoride and xenon tetrafluoride both may cause explosion in contact with acetone, aluminium, pentacarbonyliron, styrene, polyethylene, lubricants, paper, sawdust, wool or other combustible materials. Their vigorous reactions with ethanol, potassium iodate or potassium permanganate are not explosive, however.

Dimethyl sulfide

Forster, A. M., *J. Chem. Soc., Dalton Trans.*, 1984, 2827

Interaction in absence of a solvent is explosive at ambient temperature.

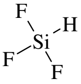
Silicon—nitrogen compounds

Gibson, J. A. *et al., Can. J. Chem.*, 1975, **53**, 3050

Interaction of xenon difluoride and dimethylaminotrimethylsilane in presence or absence of solvent became explosive at sub-zero temperatures.

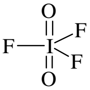
See Xenon tetrafluoride
See other NON-METAL HALIDES, XENON COMPOUNDS

†4327. Trifluorosilane
[13465-71-9] **F_3HSi**



See other HALOSILANES

4328. Iodine dioxide trifluoride
[25402-50-0] **F_3IO_2**

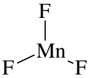


Organic materials

1. Engelbrecht, A. *et al., Angew. Chem. (Intern. Ed.)*, 1969, **8**, 769
2. Boatz, J. A. et al., *Inorg. Chem.*, 2003, **42**(17), 5282

It ignites in contact with flammable organic materials [1]. Condensing it onto acetonitrile can cause explosions above the melting point of that solvent [2].
See other HALOGEN OXIDES, IODINE COMPOUNDS, OXIDANTS

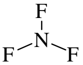
4329. Manganese trifluoride
[7783-53-1] **F_3Mn**



Glass

Mellor, 1942, Vol. 12, 344
When heated in contact it attacks glass violently, silicon tetrafluoride being evolved. It is a powerful fluorinating agent.
See other GLASS INCIDENTS, METAL HALIDES

4330. Nitrogen trifluoride
[7783-54-2] **F_3N**



Bromotrifluoromethane, Ethylene

Wyatt, J. R., *Chem. Abs.*, 1982, **97**, 75008

The presence of the halocarbon extinguishant significantly reduces the severity of the explosive oxidation of ethylene.

Charcoal

Massonne, J. *et al., Angew. Chem. (Intern. Ed.)*, 1966, **5**, 317

Adsorption of nitrogen trifluoride on to activated granular charcoal at —100°C caused an explosion, attributed to the heat of adsorption not being dissipated on the porous solid and causing decomposition to nitrogen and carbon tetrafluoride. No reaction occurs at +100°C in a flow system, but incandescence occurs at 150°C.

Chlorine dioxide

Lawless, 1968, 171

Interaction in the gas phase is explosive.

Diborane

Lawless, 1968, 34—35

No interaction occurred at ambient temperature and at pressures up to 8 bar, but violent explosions occurred at low temperatures in the liquid phase, even in absence of the impurity oxygen difluoride.

Hydrogen-containing materials.

1. Ruff., O., *Z. Angew. Chem.*, 1929, **42**, 807
2. Hoffman, C. J. *et al., Chem. Rev.*, 1962, **62**, 4

Sparking of mixtures with ammonia or hydrogen causes violent explosions, and with steam, feeble ones [1]. Mixtures with ethylene, methane and hydrogen sulfide (also carbon monoxide) explode on sparking [2].

Metals

Richter, R. F. *et al., Chem. Health & Safety*, 1995, **2**(2), 18

It is claimed that in storage nitrogen fluoride can slowly react with metals, including stainless steel, to generate tetrafluorohydrazine.

See Tetrafluorohydrazine, and next below

Tetrafluorohydrazine

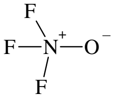
MCA Case History No. 683

A crude mixture of the 2 compounds, kept for 3 days in a stainless steel cylinder, exploded violently during valve manipulation.

See other N-HALOGEN COMPOUNDS

4331. Trifluoroamine oxide

[13847-65-9] **F_3NO**



1. Gupta, O. D. *et al., Inorg. Chem.*, 1990, **29**(3), 573

2. Gupta, O. D. *et al., Inorg. Chem.*, 2000, **39**(1), 117

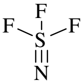
A strong oxidant, mixtures with both organic and inorganic compounds are potentially explosive. It is recommended that the synthesis be not scaled up and be performed with due safety precautions [1]. Addition to olefins can prove explosive, especially those bearing hydrogen. It was actually enones reported, 5-substituted pyrimidine-2,4-diones, on which a 6 alkoxy substituent was to be placed by the oxide and corresponding alkanol under base catalysis [2].

See AMINE OXIDES

See other *N*-HALOGEN COMPOUNDS, N—O COMPOUNDS, OXIDANTS

4332. Trifluorosulfur nitride

[15930-75-3] **F_3NS**



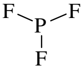
Chlorine fluoride

See Chlorine fluoride: Trifluorosulfur nitride

See other NITRIDES, NON-METAL HALIDES, N—S COMPOUNDS

4333. Phosphorus trifluoride

[7783-55-3] **F_3P**



Borane

See Borane—phosphorus trifluoride

Dioxygen difluoride

See Dioxygen difluoride: Various materials

Fluorine

See Fluorine: Covalent halides

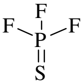
Hexafluoroisopropylideneaminolithium

See Hexafluoroisopropylideneaminolithium: Non-metal halides

See other HALOPHOSPHINES, NON-METAL HALIDES

4334. Thiophosphoryl fluoride

[2404-52-6] **F_3PS**



Air, or Sodium

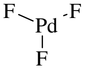
Mellor, 1940, Vol. 8, 1072—1073

In contact with air, the fluoride ignites or explodes, depending on contact conditions. Heated sodium ignites in the gas.

See related NON-METAL HALIDES

4335. Palladium trifluoride

[13842-82-5] **F_3Pd**



Hydrogen

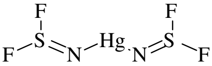
Sidgwick, 1950, 1574

Contact with hydrogen causes the unheated fluoride to be reduced incandescently.

See other METAL HALIDES

4336. Bis-*N*(imidosulfurdifluoridato)mercury

[23303-78-8] **$F_4HgN_2S_2$**



Preparative hazard

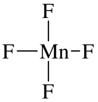
Mews, R. *et al., Inorg. Synth.*, 1986, 24, 14—16

By-products formed during the preparation of the title compound from (fluorocarbonyl)iminosulfur difluoride, mercury(II) fluoride and bromine often react violently with water: cleaning of equipment should initially be effected with carbon tetrachloride.

See other MERCURY COMPOUNDS, N—S COMPOUNDS

4337. Manganese tetrafluoride

[15195-58-1] **F_4Mn**



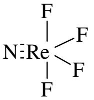
Petroleum oil

Sorbe, 1968, 84

Interaction leads to fire.

See other METAL HALIDES, OXIDANTS

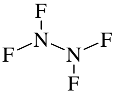
4338. Rhenium nitride tetrafluoride
[84159-29-5] **F_4NRe**



Preparative hazard

See Trimethylsilyl azide: Rhenium hexafluoride
See other NITRIDES
See related METAL HALIDES

†4339. Tetrafluorohydrazine
[10036-47-2] **F_4N_2**



1. Logothetis, A. L., *J. Org. Chem.*, 1966, **31**, 3686, 3689
2. Modica, A. P. *et al., Rept. No. 357-275*, Princetown Univ., 1963
3. Martin, K. J., *J. Amer. Chem. Soc.*, 1965, **87**, 394
4. Richter, M. F. *et al., Chem. Health & Safety*, 1995, **2**(2), 18

General precautions for use of the explosive gas tetrafluorohydrazine and derived reaction products include: reactions on as small a scale as possible and behind a barricade; adequate shielding during work-up of products because explosions may occur; storage of tetrafluorohydrazine at —80°C under 1—2 bar pressure in previously fluorinated Monel or stainless steel cylinders with Monel valves; distillation of volatile difluoroamino products in presence of an inert halocarbon oil to prevent explosions in dry distilling vessels [1]. Light-initiated explosion of the gas has been reported [2], and it explodes on contact with air and combustible vapours, so careful inerting is essential [3]. Disposal of some aged tetrafluorohydrazine cylinders is described, by puncturing the cylinder with explosives in a pit full of lime [4].

Alkenyl nitrates

Reed, S. F. *et al., J. Org. Chem.*, 1972, **37**, 3329

The products of interaction of tetrafluorohydrazine and alkenyl nitrates, bis(difluoroamino)alkyl nitrates, are heat- and impact-sensitive explosives.

See other DIFLUOROAMINO COMPOUNDS

Hydrocarbons

Petry, R. C. *et al., J. Org. Chem.*, 1967, **32**, 4034

Mixtures are potentially highly explosive, approaching the energy of hydrogen—oxygen systems.

Hydrocarbons, Oxygen

See Oxygen: Hydrocarbons, Promoters

Hydrogen

Kuhn, L. P. *et al., Inorg. Chem.*, 1970, **9**, 602

Explosive interaction is rather unpredictable, the initiation temperature required (20—80°C) depending on the condition of the vessel wall.

Nitrogen trifluoride

See Nitrogen trifluoride: Tetrafluorohydrazine

Organic materials

Reed, S. F., *J. Org. Chem.*, 1968, **33**, 2634

Mixtures with organic materials in presence of air constitute explosion hazards. Appropriate precautions are essential.

Ozone

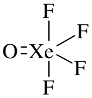
Sessa. P. A. *et al., Inorg. Chem.*, 1971, **10**, 2067

When tetrafluorohydrazine was pyrolysed at 310°C to generate NF_2 radicals and the mixture contacted liquid ozone at —196°C, a violent explosion occurred.

See other DIFLUOROAMINO COMPOUNDS, N-HALOGEN COMPOUNDS

4340. Xenon tetrafluoride oxide

[13774-85-1] **F_4OXe**



Caesium nitrate

Christe, K. O., *Inorg. Chem.*, 1988, **27**, 3763

In the preparation of xenon difluoride dioxide from caesium nitrate and xenon tetrafluoride oxide, the latter must always be used in excess to prevent formation of explosive xenon trioxide.

See Xenon trioxide, below

Graphite, Potassium iodide, Water

Selig, H. *et al., Inorg. Nucl. Chem. Lett.*, 1975, **11**, 75—77

The graphite—xenon tetrafluoride oxide intercalation compound exploded in contact with potassium iodide solution.

Polyacetylene

Selig, H. *et al., J. Chem. Soc., Chem. Comm.*, 1981, 1288

During doping of polyacetylene films, contact with the liquid tetrafluoride led to ignition of the film.

Preparative hazard

See Xenon hexafluoride: Silicon dioxide

Xenon hexafluoride: Caesium nitrate

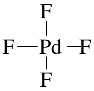
Xenon trioxide

Christe, K. O., *Inorg. Chem.*, 1988, **27**, 3763

Liquid mixtures of the 2 xenon compounds, cooled in liquid nitrogen, tend to flash, then explode after a few seconds.
See other OXIDANTS, XENON COMPOUNDS

4341. Palladium tetrafluoride

[13709-55-2] **F_4Pd**



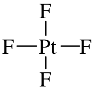
$F-\overset{F}{\underset{F}{Pd}}-F$

Water

Bailar, 1973, Vol. 3, 1278
Interaction is violent.
See other METAL HALIDES

4342. Platinum tetrafluoride

[13455-15-7] **F_4Pt**



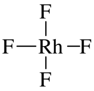
$F-\overset{F}{\underset{F}{Pt}}-F$

Water

Sidgwick, 1950, 1614
Interaction is violent.
See other METAL HALIDES

4343. Rhodium tetrafluoride

[60617-65-4] **F_4Rh**



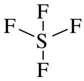
$F-\overset{F}{\underset{F}{Rh}}-F$

Water

Bailar, 1973, Vol. 3, 1235
Interaction is violent.
See other METAL HALIDES

4344. Sulfur tetrafluoride

[7783-60-0] **F_4S**



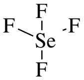
Dioxygen difluoride
See Dioxygen difluoride: Various materials
See other NON-METAL HALIDES

2-(Hydroxymethyl)furan, Triethylamine
Jenzen, A. F. *et al., J. Fluorine Chem.*, 1988, **38**, 205—208
Reaction of sulfur tetrafluoride with 2-hydroxymethylfuran in presence of triethylamine at —50°C is explosive in absence of a solvent.
See other HALOGENATION INCIDENTS

2-Methyl-3-butyn-2-ol
Boswell, G. A. *et al., Org. React.*, 1974, **21**, 8
Interaction at —78°C is explosively vigorous.

4345. Selenium tetrafluoride

[13465-66-2] **F_4Se**

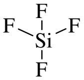


Chlorine trifluoride
Olah, G. A. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 927
The tetrafluoride is prepared by interaction of chlorine trifluoride and selenium in selenium tetrafluoride as solvent. The crude tetrafluoride must be substantially free from excess chlorine trifluoride to avoid danger during subsequent distillation at 106°C/1 bar.

Water
Aynsley, E. E. *et al., J. Chem. Soc.*, 1952, 1231
Interaction is violent.
See other NON-METAL HALIDES

4346. Silicon tetrafluoride

[7783-61-1] **F_4Si**

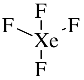


Lithium nitride
See Lithium nitride: Silicon tetrafluoride

Sodium
See Sodium: Non-metal halides (reference 8)
See other NON-METAL HALIDES

4347. Xenon tetrafluoride

[13709-61-0] **F_4Xe**



1. Shieh, J. C. *et al., J. Org. Chem.*, 1970, **35**, 4022
2. Malm, J. G. *et al., Inorg. Synth.*, 1966, **8**, 254
3. Chernick, C. L., *J. Chem. Educ.*, 1966, **43**, 619
4. Holloway, J. H., *Talanta*, 1967, **14**, 871
5. Falconer, E. E. *et al., J. Inorg. Nucl. Chem.*, 1967, **29**, 1380

Moisture converts it to highly shock-sensitive xenon oxides [1]. Precautions necessary for various aspects of its use and application are detailed [2,1,1,5].

See Xenon trioxide

Flammable materials

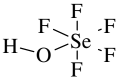
Klimov, B. D. *et al., Chem. Abs.*, 1970, **72**, 85784

Xenon tetrafluoride (or the difluoride, or their mixtures) could not be caused to detonate by impact. Xenon difluoride and xenon tetrafluoride both may cause explosion in contact with acetone, aluminium, pentacarbonyliron, styrene, polyethylene, lubricants, paper, sawdust, wool or other combustible materials. Their vigorous reactions with ethanol, potassium iodate or potassium permanganate are not explosive, however.

See other NON-METAL HALIDES, OXIDANTS, XENON COMPOUNDS

4348. Pentafluoroorthoselenic acid

[38989-47-8] **F_5HOSe**



Preparative hazard

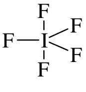
See Fluorine: Hydrogen fluoride, Seleninyl fluoride

See other INORGANIC ACIDS

See related NON-METAL HALIDES

4349. Iodine pentafluoride

[7783-66-6] **F_5I**



Benzene

Ruff, O. *et al., Z. Anorg. Chem.*, 1931, **201**, 245

Interaction becomes violent above 50°C.

Calcium carbide, or Potassium hydride

Booth, H. S. *et al., Chem. Rev.*, 1947, **41**, 425

Both incandesce on contact, the carbide when warmed.

Diethylaminotrimethylsilane

Oates, G. *et al., J. Chem. Soc., Dalton Trans.*, 1974, 1383

A mixture exploded at around —80°C. Reactions with other silanes were very exothermic.

Dimethyl sulfoxide

Lawless, E. M., *Chem. Eng. News*, 1969, **47**(13), 8, 109

Unmoderated reaction with the sulfoxide is violent, and in the presence of diluents the reaction may be delayed and become explosively violent. Although small-scale reactions were uneventful, reactions involving about 0.15 g mol of the pentafluoride and sulfoxide in presence of trichlorotrifluoromethane or tetrahydrothiophene-1,1-dioxide as diluents caused delayed and violent explosions. Silver difluoride and other fluorinating agents also react violently with the sulfoxide.

See Dimethyl sulfoxide: Acyl halides, etc.

See other INDUCTION PERIOD INCIDENTS

Limonene, Tetrafluoroethylene

See Tetrafluoroethylene: Iodine pentafluoride, etc.

Metals, or Non-metals

1. Sidgwick, 1950, 1159
2. Mellor, 1940, Vol. 2, 114
3. Booth, H. S. *et al., Chem. Rev.*, 1947, **41**, 424—425

Contact with boron, silicon, red phosphorus, sulfur, or arsenic, antimony or bismuth usually causes incandescence [1]. Solid potassium or molten sodium explode with the pentafluoride, and aluminium foil ignites on prolonged contact [2]. Molybdenum and tungsten incandesce when warmed [3].

Organic materials, or Potassium hydroxide

Pascal, 1960, Vol. 16.1, 582

The pentafluoride chars and usually ignites organic materials, and interaction with potassium hydroxide is violently exothermic.

Tetraiodoethylene

Mellor, 1956, Vol. 2, Suppl. 1, 176

Rapid mixing leads to explosion.

Water

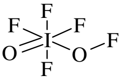
Ruff, O. *et al., Z. Anorg. Chem.*, 1931, **201**, 245

Reaction with water or water-containing materials is violent.

See other INTERHALOGENS, IODINE COMPOUNDS

4350. Tetrafluoroiodosyl hypofluorite

[72151-31-6] **F_5IO_2**



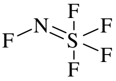
Christe, K. O. *et al., Inorg. Chem.*, 1981, **20**, 2105

Two explosions were encountered in reactions involving the hypofluorite.

See other HALOGEN OXIDES, HYPOHALITES, IODINE COMPOUNDS

4351. *N*-Fluoroiminosulfur tetrafluoride

[74542-20-4] **F_5NS**



Alone, or Peroxydisulfuryl difluoride

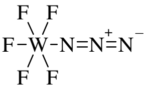
O'Brien, B. A. *et al., Inorg. Chem.*, 1984, **23**, 2189

Samples of the *N*-fluoro compound, either alone or in admixture with the difluoride, exploded forcefully while warming from —196°C to +22°C. Sample size should not exceed 3 mmol.

See other N-HALOGEN COMPOUNDS, N—S COMPOUNDS

4352. Azidopentafluorotungsten

[75900-58-2] **F_5N_3W**



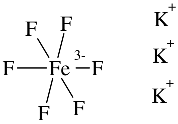
Fawcett, J. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 2294—2296

Trimethylsilyl azide reacts with excess tungsten hexafluoride in solvent to give the title compound, which explodes at 63°C or if dried in dynamic vacuum. A deficiency of the hexafluoride gave a mixture (presumably containing poly-azides) which exploded at ambient temperature.

See other METAL AZIDE HALIDES

4353. Tripotassium hexafluoroferrate(3-)

[13815-30-0] **F_6FeK_3**

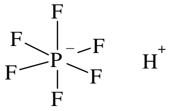


Wright, S. W., *J. Chem. Educ.*, 1994, **71**(3), 251

The anhydrous salt will undergo a 'thermite' reaction with aluminium to produce molten iron.

See other THERMITE REACTIONS

4354. Hydrogen hexafluorophophosphate (Hexafluorophosphoric acid)
[16940-81-1] (anhydrous) **F_6HP**



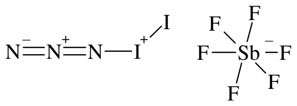
Borosilicate glass

1. Pearse, G. A., *Chem. Brit.*, 1989, **25**, 30
2. Woolf, A. A., *Chem. Brit.*, 1989, **25**, 361

Copper(II) hexafluorophosphate was being prepared by adding 60—65% aqueous acid to aqueous copper carbonate, followed by evaporation of the reaction mixture at 80—90°C by heating on a ceramic hotplate. During evaporation, the Pyrex vessel was dissolved at the liquid level, and the leaking solution also dissolved the ceramic hotplate. This was attributed to presence of hydrofluoric acid, arising from hydrolysis of the fluorophosphoric acid. Teflon-lined vessels are recommended for such operations [1]. Aqueous solutions contain but little of the acid, in hydrolytic equilibrium with mono- and di-fluorophophoric acids, orthophosphoric acid and hydrofluoric acid, and such a mixture is clearly incompatible with glass containers, and warnings have been published. Anhydrous hexafluorophosphate salts may be prepared in glass by metathesis in anhydrous solvents [2].

See other GLASS INCIDENTS, INORGANIC ACIDS

4355. Azidoiodoiodonium hexafluoroantimonate
[ ] **$F_6I_2N_3Sb$**

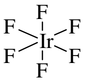


Schleyer, P. von R. *et al., Angew. Chem. (Int.)*, 1992, **31**(10), 1338

This compound, which is more sensitive than iodonium azide, can explode spontaneously below —20°C. It is the first known I—N containing cationic species.

See other N-HALOGEN COMPOUNDS, IODINE COMPOUNDS, NON-METAL AZIDES

4356. Iridium hexafluoride
[7783-75-7] **F_6Ir**



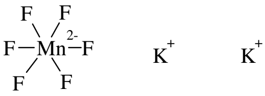
Silicon

See Silicon: Metal hexafluorides

See other METAL HALIDES, OXIDANTS

4357a. Potassium hexafluoromanganate(IV)

[16962-31-5] **F_6K_2Mn**



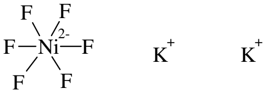
Preparative hazard

See Potassium permanganate: Hydrofluoric acid

See related METAL HALIDES

4357b. Dipotassium hexafluoronickelate(IV)

[17218-47-2] **F_6K_2Ni**

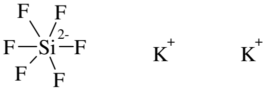


Michl, J. *et al., J. Amer. Chem. Soc.*, 2000, **122**, 10255

This potent fluorinating agent may explode on contact with oxidisable substrates, including water.

4358. Potassium hexafluorosilicate(2—)

[16871-90-2] **F_6K_2Si**



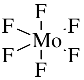
Hydrogen fluoride

See Hydrogen fluoride: Potassium tetrafluorosilicate(2—)

See related NON-METAL HALIDES

4359. Molybdenum hexafluoride

[7783-77-9] **F_6Mo**



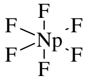
Tetramethoxysilane

See Tetramethoxysilane: Metal hexafluorides

See other METAL HALIDES

4360. Neptunium hexafluoride

[14521-05-2] **F_6Np**



Water

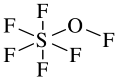
Bailar, 1973, Vol. 5, 168

Interaction with water at ambient temperature is violent.

See other METAL HALIDES, OXIDANTS

4361. Pentafluorosulfur hypofluorite

[15179-32-5] **F_6OS**



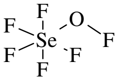
Ruff, J. K., *Inorg. Synth.*, 1968, **11**, 137

It is considered to be potentially explosive.

See other HYPOHALITES

4362. Pentafluoroselenium hypofluorite

[27218-12-8] **F_6OSe**



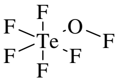
1. Mitra, G. *et al., J. Amer. Chem. Soc.*, 1959, **81**, 2646
2. Smith, J. E. *et al., Inorg. Chem.*, 1970, **9**, 1442

A cooled sample exploded when allowed to dry rapidly [1], but this may have been owing to impurities, as it did not happen in the later work [2].

See other HYPOHALITES

4363. Pentafluorotellurium hypofluorite

[83314-21-0] **F_6OTe**



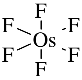
Christe, K. O. *et al., Inorg. Chem.*, 1987, **26**, 920

A shock-sensitive explosive, which needs full handling precautions.

See other HYPOHALITES

4364. Osmium hexafluoride

[13768-38-2] **F_6Os**



Organic materials

Sorbe, 1968, 91

It causes ignition of paraffin oil and other organic materials.

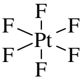
Silicon

See Silicon: Metal hexafluorides

See other METAL HALIDES, OXIDANTS

4365. Platinum hexafluoride

[13693-05-5] **F_6Pt**



Bis(trifluoromethyl) nitroxide

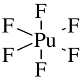
Christe, K. O. *et al., J. Fluorine Chem.*, 1974, **4**, 425

Interaction of the nitroxide radical and this powerful oxidant was very violent during warming from —196°C.

See other METAL HALIDES, OXIDANTS

4366. Plutonium hexafluoride

[13693-06-6] **F_6Pu**



Water

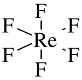
Bailar, 1973, Vol. 5, 168

Interaction with water at ambient temperature is violent.

See other METAL HALIDES, OXIDANTS

4367. Rhenium hexafluoride

[10049-17-9] **F_6Re**



Silicon

See Silicon: Metal hexafluorides

Tetramethoxysilane

See Tetramethoxysilane: Metal hexafluorides

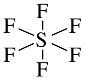
Trimethylsilyl azide

See Trimethylsilyl azide: Rhenium hexafluoride

See other METAL HALIDES, OXIDANTS

4368. Sulfur hexafluoride

[2551-62-4] **F_6S**



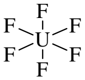
Disilane

See Disilane: Non-metal halides, etc.

See other NON-METAL HALIDES

4369. Uranium hexafluoride

[7783-81-5] **F_6U**



Aromatic hydrocarbons, or Hydroxy compounds

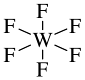
Sidgwick, 1950, 1072

Interaction with benzene, toluene, or xylene is very vigorous, with separation of carbon, and violent with ethanol or water.

See other METAL HALIDES, OXIDANTS

4370. Tungsten hexafluoride

[7783-82-6] **F_6W**



Aitchison, K. A. *et al., Chem. Abs.*, 1987, **106**, 147494

Safety procedures for use of tungsten hexafluoride in CVD processing operations are emphasized.

Tetramethoxysilane

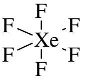
See Tetramethoxysilane: Metal hexafluorides

Trimethylsilyl azide

See Azidopentafluorotungsten

See other METAL HALIDES, OXIDANTS

4371. Xenon hexafluoride
[13693-09-9] **F_6Xe**



Caesium nitrate

Christe, K. O., *Inorg. Chem.*, 1988, **27**, 3763

In the preparation of xenon tetrafluoride oxide from the hexafluoride and caesium nitrate, the former must always be used in excess to prevent formation of explosive xenon trioxide.

See Xenon tetrafluoride oxide: Xenon trioxide

Fluoride donors, Water

Bailar, 1973, Vol. 1, 317

Adducts of the hexafluoride with sodium fluoride, potassium fluoride, rubidium fluoride, caesium fluoride or nitrosyl fluoride react violently with water.

Hydrogen

Malm, J. G. *et al., J. Amer. Chem. Soc.*, 1963, **85**, 110

Interaction is violent.

Silicon dioxide

1. McKee, D. E. *et al., Inorg. Chem.*, 1973, **12**, 1722
2. Aleinikov, N. N. *et al., J. Chromatog.*, 1974, **89**, 367

Interaction of the yellow hexafluoride with silica to give xenon tetrafluoride oxide must be interrupted before completion (disappearance of colour) to avoid the possibility of formation and detonation of xenon trioxide [1]. An attempt to collect the hexafluoride in fused silica traps at —20°C after separation by preparative gas chromatography failed because of reaction with the silica and subsequent explosion of the oxygen compounds of xenon so produced [2].

See Xenon trioxide

Water

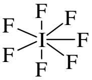
1. Gillespie, R. J. *et al., Inorg. Chem.*, 1974, **13**, 2370—2374
2. Schumacher, G. A. *et al., Inorg. Chem.*, 1984, **23**, 2923

Although uncontrolled reaction of xenon hexafluoride and moisture produces explosive xenon trioxide, controlled action by progressive addition of limited amounts of water vapour with agitation to a frozen solution of the hexafluoride in anhydrous hydrogen fluoride at —196°C to give xenon oxide tetrafluoride or xenon dioxide difluoride is safe [1]. Controlled hydrolysis in solution in hydrogen fluoride is, however, described as hazardous [2].

See other NON-METAL HALIDES, OXIDANTS, XENON COMPOUNDS

4372. Iodine heptafluoride

[16921-96-3] **F_7I**



Carbon, or Combustible gases

Booth, H. S. *et al., Chem. Rev.*, 1947, **41**, 428

Activated carbon ignites immediately in the gas, mixtures with methane ignite, and those with carbon monoxide ignite on warming, while those with hydrogen explode on heating or sparking.

Metals

Booth, H. S. *et al., Chem. Rev.*, 1947, **41**, 427

Interaction with barium, potassium and sodium is immediate, accompanied by evolution of light and heat. Aluminium, magnesium, and tin are passivated on contact, but on heating react similarly to the former metals.

Organic solvents

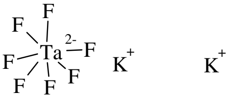
Booth, H. S. *et al., Chem. Rev.*, 1947, **41**, 428

Benzene, light petroleum, ethanol and ether ignite in contact with the gas, while the exotherm with acetic acid, acetone or ethyl acetate causes rapid boiling. General organic materials (cellulose, grease, oils) ignite if excess heptafluoride is present.

See other INTERHALOGENS

4373. Potassium heptafluorotantalate(V)

[16924-00-8] **F_7K_2Ta**



Water

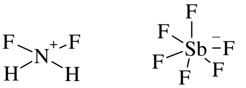
Ephraim, 1939, 353

Hydrolysis is less violent than that of tantalum pentafluoride.

See related METAL HALIDES

4374. Difluoroammonium hexafluoroantimonate

[56533-31-4] **F_8H_2NSb**

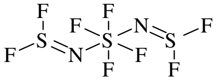


See Difluoroammonium hexafluoroarsenate

See related N-HALOGEN COMPOUNDS

4375. Bis(*S,S*-difluoro-*N*-sulfimido)sulfur tetrafluoride

[52795-23-0] $F_8N_2S_3$



Water

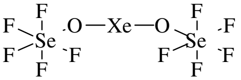
Hofer, R. *et al., Angew, Chem. (Intern. Ed.)*, 1973, **12**, 1000

Either the liquid tetrafluoride or its viscous polymer decomposes explosively in contact with water.

See other NON-METAL HALIDES, N—S COMPOUNDS

4376. Xenon(II) pentafluoroorthoselenate

[38344-58-0] $F_{10}O_2Se_2Xe$



Oxidisable materials

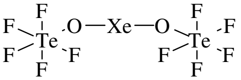
Seppelt, K., *Angew. Chem. (Intern. Ed.)*, 1972, **11**, 724

Interaction is explosive.

See other OXIDANTS, XENON COMPOUNDS

4377. Xenon(II) pentafluoroorthotellurate

[25005-56-5] $F_{10}O_2Te_2Xe$



Organic solvents

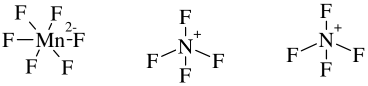
Sladky, F., *Angew. Chem. (Intern. Ed.)*, 1969, **8**, 523; *Inorg. Synth.*, 1986, **24**, 36

Explosive or very vigorous reactions occur on contact with acetone, benzene or ethanol.

See other OXIDANTS, XENON COMPOUNDS

4378. Tetrafluoroammonium hexafluoromanganate

[74449-37-9] $F_{14}MnN_2$



Water

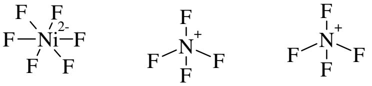
Christe, K. O. *et al., Inorg. Chem.*, 1980, **19**, 3254

Reaction of the powerful oxidant with water is extremely violent and needs proper precautions. In absence of fuels, it is not shock-sensitive.

See other N-HALOGEN COMPOUNDS, OXIDANTS

4379. Tetrafluoroammonium hexafluoronickelate

[63105-40-8] **$F_{14}N_2Ni$**



Christe, K. O., US Pat. 4 108 965, 1978

This high energy oxidant is useful in propellants.

Water

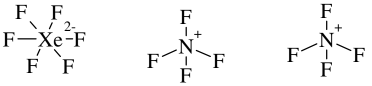
Christe, K. O., *Inorg. Chem.*, 1977, **16**, 2238

The hydrolysis of this powerful oxidant is very violent, and may be explosive if attempted appreciably above —180°C.

See other N-HALOGEN COMPOUNDS, OXIDANTS

4380. Tetrafluoroammonium octafluoroxenate

[82963-15-3] **$F_{16}N_2Xe$**



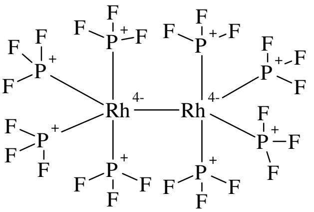
Christe, K. O. *et al.*, US Pat. 4 447 407, 1984

It produces the highest theoretical detonation pressures in explosive formulations (maximal yields of fluorine and nitrogen trifluoride).

See other N-HALOGEN COMPOUNDS, OXIDANTS, XENON COMPOUNDS

4381. Octakis(trifluorophosphine)dirhodium

[14876-96-1] **$F_{24}P_8Rh_2$**



Acetylenic esters

Bennett, M. A. *et al., Inorg. Chem.*, 1976, **15**, 107—108

Formation of complexes with excess methyl propiolate or dimethyl acetylenedicarboxylate must not be allowed to proceed at above +20°C, or violently explosive polymerisation of the acetylene esters will occur.
See other POLYMERISATION INCIDENTS

4382. Iron
[7439-89-6] **Fe**

Fe

1. Bailar, 1973, Vol. 3, 985
2. Gusein, M. A. *et al., Chem. Abs.*, 1974, **81**, 124774
3. Jakusch, H. *et al., Chem. Abs.*, 1983, **98**, 130471
4. Brinza, V. N. *et al., Chem. Abs.*, 1983, **99**, 7872
5. Bandyopadhyay, A. *et al., Steel India*, 1987, **10**, 58—63
6. Ganguly, A. *et al., Tool Alloy Steels*, 1988, **22**(1), 19—26

The known pyrophoric [1] and explosive properties of ultrafine iron powder were examined in detail [2]. Pyrophoric iron particles may be stabilised by heat treatment with oxygen-containing gases in 2 stages at 25—45°, then 50—70°C [3]. The ignition temperature of sponge iron (183—203°C) is independent of heating rate and coincides with the dissociation temperature of iron hydroxides formed on the surface [4]. An incident involving spontaneous combustion of hydrogen-reduced sponge iron (Direct Reduced Iron, DRI) is analysed. The surface area and porosity of coal-reduced DRI prepared at over 1000°C is lower, and the product, a more dense, sintered DRI has greater oxidation resistance. Fire control and salvage techniques are discussed [5]. Other aspects of storing, handling and shipping of sponge iron are reviewed [6].
See entry HIGH SURFACE-AREA SOLIDS
See other PYROPHORIC METALS

Acetaldehyde
See Acetaldehyde: Metals

Air, Oil
Glaser, A., *Arbeitschutz*, 1941, 134—135
Oxidative heating of oily iron dust in a collecting vessel caused vaporisation of oil and subsequent ignition, causing an explosion.
See other SELF-HEATING AND IGNITION INCIDENTS

Air, Water

1. Brimelow, H. C., private comm., 1972
2. Unpublished observations, 1949

2-Nitrophenylpyruvic acid was reduced to oxindole using iron pin-dust—ferrous sulfate in water. The iron oxide—iron residues, after filtering and washing with chloroform, rapidly heated in contact with air and shattered the Buchner funnel [1]. Previously, rapid heating effects had been observed on sucking air through the iron oxide residues from hot filtration of aqueous liquor from reduction of a nitro compound with reduced iron powder [2].
See Water, below

Chloric acid
See Chloric acid: Metals, etc.

Chloroformamidinium nitrate
See Chloroformamidinium nitrate: Alone, etc.

Halogens or Interhalogens MRH values show % of halogen
See Bromine pentafluoride: Acids, etc. MRH 4.23/54
Chlorine trifluoride: Metals
Chlorine: Metals MRH 2.68/56
Fluorine: Metals MRH 7.49/40

Other reactants
Yoshida, 1980, 233
MRH values calculated for 19 combinations with oxidants are given.

Oxidants MRH values show % of oxidant
See Halogens or Interhalogens above
Ammonium nitrate: Metals MRH 3.35/68
Ammonium peroxodisulfate: Iron MRH 0.92/78
Dinitrogen tetraoxide: Metals MRH 4.43/38
Hydrogen peroxide: Metals MRH 4.60/48
Nitryl fluoride: Metals
Peroxyformic acid MRH 5.69/99+
Potassium dichromate: Iron MRH 0.42/66
Potassium perchlorate: Metal powders
Sodium peroxide: Metals MRH 1.55/68

Polystyrene
Unpublished observation, 1971
Iron flake powder and polystyrene beads had been blended in a high-speed mixer. The mixture ignited and burned rapidly when discharged into a polythene bag. Rapid oxidation of the finely divided metal and/or static discharge may have initiated the fire. No ignition occurred when the iron powder was surface coated with stearic acid.
See other STATIC INITIATION INCIDENTS

Sodium acetylide
See Sodium acetylide: Metals

Water
1. Asakura, S. *et al., Chem. Abs.*, 1983, **99**, 110033
2. Anon, *Safety Digest Univ. Safety Assoc.*, 1991, **41**, 10
3. Clancey, V. J., *Proc. 41st Ironmaking Conf.*, 1982, 244—250

In a study of the spontaneous exothermic reaction of iron powder or turnings with water in absence of chlorides, rust was found to catalyse the reaction [1]. On drilling holes into steel tubes filled with possibly wet ferrous scrap and sealed some years, they were found to be pressurised. The third tube produced an explosion and jet of flame causing some injury to the driller. This was probably attributable to hydrogen generation [2]. Hazards associated with shipping of direct-reduced iron and arising

from reactivity with condensation etc. in ship's holds, with liberation and ignition of hydrogen, are discussed [3].
See Air, Water, above
See other CORROSION INCIDENTS, GAS EVOLUTION INCIDENTS, METALS

4383. Ferromanganese (Iron—manganese alloy)
[73202-12-7] **Fe—Mn**

Fe—Mn

See entry FERROALLOY POWDERS
See other ALLOYS

4384. Ferrosilicon (Iron—silicon alloy)
[50645-52-8] **Fe—Si**

Fe—Si

1. Delyan, V. I. *et al., Chem. Abs.*, 1983, **99**, 25024
2. Babaitsev, I. V. *et al., Chem. Abs.*, 1987, **107**, 241804

The flammability and explosive hazard of ferrosilicon powder is increased substantially during grinding in a vibratory mill [1]. Explosion hazards from air—hydrogen, —acetylene, or —propane mixtures formed during preparation of ferrosilicon containing alkaline earth additives are attributed to contact of barium or magnesium carbide or silicide additive with atmospheric moisture [2].
See FERROALLOY POWDERS

Sodium hydroxide, Water
Kirk-Othmer (3rd edn.), 1982, Vol. 19, 494
Intimate mixtures of ferrosilicon with solid sodium hydroxide incandesce when moistened.

Water
1. Anon., *Chem. Trade J.*, 1956, **139**, 1180
2. Horn, Q.C. *et al., Chem. Abs.* 1998, **128**, 37646c; 37653c
3. Horn, Q.C. *et al., Chem. Abs.*, 1999, **131**, 202612k

Ferrosilicon containing 30—75% of silicon is hazardous, particularly when finely divided, and must be kept in a moisture-tight drum. In contact with water, the impurities present (arsenide, carbide, phosphide) evolve extremely poisonous arsine, combustible acetylene and spontaneously flammable phosphine [1 & 2]. The level of phosphine (and presumably the other hydrides) produced depends upon presence of Al, Ca, and Mg impurities. The relationship is not simple [3].
See related METAL NON-METALLIDES

4385. Ferrotitanium (Iron—titanium alloy)

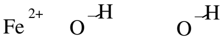
[87490-22-0] **Fe—Ti**

Fe —Ti

See entry FERROALLOY POWDERS
See other ALLOYS

4386. Iron(II) hydroxide

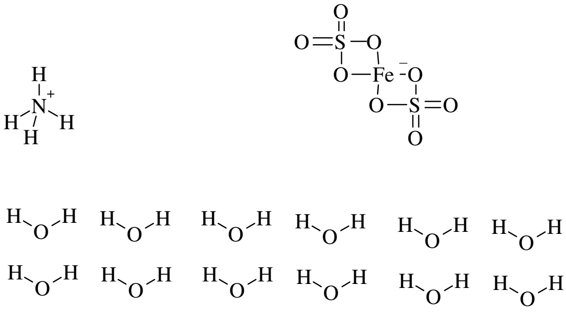
[18624-44-7] **FeH_2O_2**



Gibson, 1969, 121
Prepared under nitrogen, it is pyrophoric in air, producing sparks.
See other PYROPHORIC MATERIALS, REDUCANTS

4387. Ammonium iron(III) sulfate

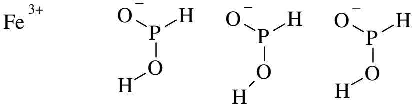
[7783-83-7] **$FeH_4NO_8S_2.12H_2O$**



Sulfuric acid
See Sulfuric acid: Ammonium iron(III) sulfate
See related METAL OXONON-METALLATES

4388. Iron(III) phosphinate

[7783-84-8] **$FeH_6O_6P_3$**



Mellor, 1981, Vol. 8, Suppl. 3, 626
It is used in impact-sensitive priming conmpositions.
See other METAL PHOSPHINATES, REDOX COMPOUNDS

4389. Iron(II) iodide

[7783-86-0] **FeI_2**

Fe^{2+} I^- I^-

Alkali metals

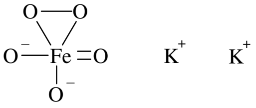
Sodium: Metal halides

See Potassium: Metal halides

See other METAL HALIDES

4390. Potassium peroxoferrate(2—)

[ ] **FeK_2O_5**



Alone, or Non-metals, or Sulfuric acid

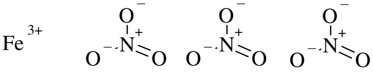
Goralevich, D. K., *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1115

It explodes on heating or impact, or in contact with charcoal, phosphorus, sulfur or sulfuric acid.

See other PEROXOACID SALTS

4391. Iron(III) nitrate

[10421-48-4] **FeN_3O_9**



Dimethyl sulfoxide

See Dimethyl sulfoxide: Metal oxosalts

See other METAL NITRATES

4392. Iron(II) oxide

[1345-25-1] **FeO**

$Fe{=}O$

1. Mellor, 1941, Vol. 13, 715
2. Bailar, 1973, Vol. 3, 1008—1009

The oxide (prepared at 300°C) burns in air above 200°C, while the finely divided oxide prepared by reduction may be pyrophoric at ambient temperature [1]. That prepared by thermal decomposition under vacuum of iron(II) oxalate is also pyrophoric [2].

Oxidants

See Nitric acid: Iron(II) oxide

Hydrogen peroxide: Metals, etc.

Sulfur dioxide

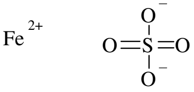
Mellor, 1941, Vol. 13, 715

The oxide incandesces when heated in sulfur dioxide.

See other METAL OXIDES, METAL OXIDES, REDUCANTS

4393. Iron(II) sulfate

[7720-78-7] **FeO_4S**



HCS 1980, 502

Arsenic trioxide, Sodium nitrate

See Sodium nitrate: Arsenic trioxide, Iron(II) sulfate

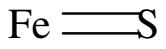
Methyl isocyanoacetate

See Methyl isocyanoacetate: Heavy metals

See other METAL OXONON-METALLATES, REDUCANTS

4394. Iron(II) sulfide

[1317-37-9] **FeS**



1. Mellor, 1942, Vol. 14, 157
2. Anon., *Chem. Age.*, 1939, **40**, 267
3. Davie, F. M. *et al., J. Loss Prev.*, 1993, **6**(3), 139 & 145
4. Walker, R. *et al., Ind. Eng. Chem. Res.*, 1996, **35**(5), 1736

The moist sulfide readily oxidises in air exothermally, and may reach incandescence. Grinding in a mortar hastens this [1]. The impure sulfide formed when steel processing equipment is used with materials containing hydrogen sulfide or volatile sulfur compounds is pyrophoric, and has caused many fires and explosions when such equipment is opened without effective purging. Various methods of purging are discussed [2]. Formation of pyrophoric FeS in bitumen tanks is considered as a cause of spontaneous ignition and explosion in the head space [3]. A detailed study of formation of possibly pyrophoric sulphides from rust in crude oil tankers has been made [4].

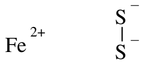
Lithium

See Lithium: Metal oxides, etc.

See other IGNITION SOURCES, METAL SULFIDES

4395. Iron disulfide (Iron pyrites)

[1309-36-0] **FeS_2**



1. Anon., *Angew. Chem. (Nachr.)*, 1954, **2**, 219
2. Bowes. P. C., *Ind. Chemist*, 1954, **30**, 12—14
3. Ruiss, I. G. *et al., J. Chem. Ind.* (Moscow), 1935, **12**, 692—696
4. Guedes de Carvalho, R. A. *et al., Chem. Abs.*, 1980, **93**, 223677

Finely powdered pyrites, especially in presence of moisture, will rapidly heat spontaneously and ignite, particularly in contact with combustible materials [1]. Inert gas blanketing will prevent this [2]. Precautions to reduce the self-ignition hazards of powdered pyrites, and the explosion hazards of pyrites— air mixtures in the furnaces of sulfuric acid plants have been detailed and discussed [3]. Further studies on minimum moisture content of Portugese pyrites for safe transportation and storage are reported [4].

See other SELF-HEATING AND IGNITION INCIDENTS

Carbon

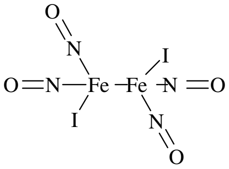
Ruiss, I. G. *et al., J. Chem. Ind.* (Moscow), 1935, **12**, 696

The presence of carbon in pyrites lowers the ignition temperature to 228—42°C and increases the explosivity of dust suspensions in air.

See other METAL SULFIDES

4396. Di-μ-iodotetranitrosyldiiron

[15002-08-1] **$Fe_2I_2N_4O_4$**



Kegzdins, P. *et al.* US Pat. 5,631,284, 1997; *Chem. Abs.*, 1997, **127**, 50793x

This compound may decompose explosively during sublimation, if overheated.

4397. Iron(III) oxide

[1309-37-1] **Fe_2O_3**

$O{=}Fe{-}O{-}Fe{=}O$

Aluminium

1. Mellor, 1946, Vol. 5, 217
2. Bodur, G. M., *J. Chem. Educ.*,1985, **62**, 1107

An intimately powdered mixture, usually ignited by magnesium ribbon as a high-temperature fuse, reacts with an intense exotherm to produce molten iron and was used formerly (before the advent of gas or arc welding) in the commercial 'thermite' welding process. Incendive particles have been produced by this reaction on impact between aluminium and rusty iron. (The term 'thermite reaction' has now been extended to include many combinations of reducing metals and metal oxides) [1]. Some accidents in demonstrating the thermite reaction are described [2].
See Aluminium: Metal oxides, etc.
See Calcium disilicide, below
See also Magnesium: Metal oxides
See also LIGHT ALLOYS
See other THERMITE REACTIONS

Aluminium, Propene
Batty, G. F., private comm., 1972
Use of a rusty iron tool on an aluminium compressor piston caused incendive sparks which ignited residual propene—air mixture in the cylinder.
See Aluminium, above

Aluminium—magnesium alloy, Water
See Aluminium—magnesium alloy: Iron(III) oxide, etc.

Aluminium—magnesium—zinc alloys
See Aluminium—magnesium—zinc alloy: Rusted steel

Calcium disilicide
Berger, E., Compt. rend., 1920, 170, 29
The mixture ('silicon thermite') attains a very high temperature when heated, producing molten iron like the usual thermite mixture.
See Aluminium, above

Carbon monoxide
Othen, C. W., *School, Sci. Rev.*, 1964, **45**(156), 459
The reason for a previously reported explosion during reduction of iron oxide with carbon monoxide is given as the formation of pentacarbonyliron at temperatures between 0 and 150°C. Suitable heating arrangements and precautions will eliminate this hazard.
See Pentacarbonyliron

Ethylene oxide
See Ethylene oxide: Contaminants

Guanidinium perchlorate
See Guanidinium perchlorate: Iron(III) oxide

Hydrogen peroxide
See Hydrogen peroxide: Metals, etc.

Magnesium

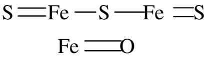
See Magnesium: Metal oxides

Metal acetylides

See Calcium acetylide: Iron(III) chloride, etc.
Caesium acetylide: Iron(III) oxide
Rubidium acetylide: Metal oxides
See other METAL OXIDES

4398. Iron(III) sulfide

[12063-27-3] **Fe_2S_3**



$S{=}Fe{-}S{-}Fe{=}S$

$Fe{=}O$

Moore, F. M., *Proc. Gas Cond. Conf.*, 1976, **26**, 1

Hydrogen sulfide is removed from natural gas by passage over iron sponge, when flammable iron sulfide is produced. Handling precautions during regeneration of the reactor beds are detailed.

See other METAL SULFIDES, PYROPHORIC IRON—SULFUR COMPOUNDS

4399. Iron(II,III) oxide ('Magnetite')

[1317-61-9] **Fe_3O_4**

$O{=}Fe{-}O{-}Fe{=}O$

Aluminium, Calcium silicide, Sodium nitrate.

Schierwater, F-W., *Sichere Chemiearb.*, 1976, **28**, 30—31

During the preparation of a foundry mixture of the finely divided oxide with aluminium powder and small amounts of sodium nitrate and calcium silicide with calcium fluoride as flux, a violent explosion occurred in the conical mixer. It had been established previously that the mixture could not be ignited by impact or friction and that if ignited by a very high-energy source (magnesium ribbon), it burned rather slowly to a glowing liquid. The possibility of ignition of the solid mixture by silane produced from water acting on the silicide content was discounted, but an aluminium dust explosion may have been involved with this ignition source.

Aluminium, Sulfur

Crozier, T. H., *HM Insp. Expl. Spec. Rept. 237*, London, HMSO, 1929

A 20 t quantity of an incendiary bomb mixture of the finely powdered oxide, aluminium and sulfur became accidentally ignited and burned with almost explosive violence. It is similar to thermite mixture.

See other THERMITE REACTIONS

Hydrogen trisulfide

See Hydrogen trisulfide: Metal oxides
See other METAL OXIDES

4400. Gallium

[7440-55-3] **Ga**

Ga

Aluminium alloys

Marshall, C., private comm., 1981

Serious problems may arise if gallium or its liquid alloys contact aluminium alloy structural components in aircraft, when rapid ‘amalgamation’ and weakening occurs.

See other CORROSION INCIDENTS

Halogens

1. Walker, H. L., *School Sci. Rev.*, 1956, **37**(132), 196
2. Bailar, 1973, Vol. 1, 1084

The metal reacts with cold chlorine strongly exothermically, and the compact metal with bromine even at —33°C, reaction being violent at ambient temperature [1]. Interaction of gallium with liquid bromine at 0°C proceeds with a flash, resembling the action of alkali metals with water [2].

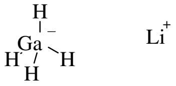
Hydrogen peroxide

See Hydrogen peroxide: Gallium, etc.

See other METALS

4401. Lithium tetrahydrogallate

[17836-90-7] **GaH_4Li**



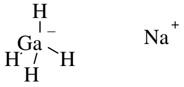
Gaylord, 1956, 26

Though of lower stability than the analogous aluminate, its reactivity is generally similar to that of the latter.

See other COMPLEX HYDRIDES

4402. Sodium tetrahydrogallate

[32106-51-7] **GaH_4Na**



Water

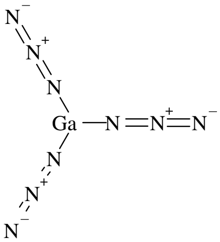
McKay, 1966, 169

It is explosively hydrolysed by water.

See other COMPLEX HYDRIDES

4403a. Gallium azide (Triazidogallane)

[ ] **GaN_9**



Fischer, R. A. *et al., Chem. Eur. J.*, 1996, **2**(11), 1353

The solid detonates violently when heated rapidly to above 280°C.

See other METAL AZIDES

4403b. Sodium tetraazidogallate

[203391-71-3] **$Ga_2N_{12}Na$**

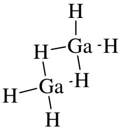
$(N_3)_4Ga^- \ Na^+$

METAL AZIDES

See SODIUM TETRAAZIDOMETALLATES

4404. Digallane

[12140-58-8] **Ga_2H_6**



Leleu, *Cahiers*, 1976, (85), 585

According to some authors it ignites in air.

See other METAL HYDRIDES

4405. Gallium(I) oxide

[12024-20-3] **Ga_2O**

$Ga^+ \quad Ga^+ \quad O^{2-}$

Bromine

Bailar, 1973, Vol. 1, 1091

It is a strong reducant, reacting violently with bromine.

See other METAL OXIDES, REDUCANTS

4406. Germanium

[7440-56-4] **Ge**

Ge

Halogens

Mellor, 1941, Vol. 7, 260

The powdered metal ignites in chlorine, and lumps will ignite on heating in chlorine or bromine.

Oxidants

Mellor, 1941, Vol. 7, 260—261

The powdered metal reacts violently with nitric acid, and mixtures with potassium chlorate or nitrate explode on heating. Heated germanium burns with incandescence in oxygen.

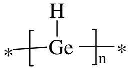
Sodium peroxide: Metals (reference 2)

See Potassium hydroxide: Germanium

See other METALS

4407. Poly(germanium monohydride)

[13572-99-1] **$(GeH)_n$**



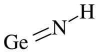
Jolly, W. L. *et al., Inorg. Synth.*, 1963, **7**, 39

The solid polymeric hydride sometimes decomposes explosively into its elements on exposure to air.

See other METAL HYDRIDES

4408. Germanium imide

[26257-00-1] **GeHN**



Air, or Oxygen

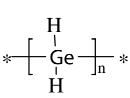
Johnson, O. H., *Chem. Rev.*, 1952, **51**, 449

On exposure to air it reacts violently, and in oxygen incandescence occurs.

See other N-METAL DERIVATIVES

4409. Poly(germanium dihydride)

[32028-94-7] **$(GeH_2)_n$**

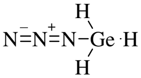


Bailar, 1973, Vol. 2, 13

Impact may cause explosive decomposition to the elements, with ignition of the liberated hydrogen.

See other METAL HYDRIDES

4410. Azidogermane
[21138-22-7] **GeH_3N_3**



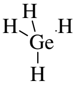
Fluorosilane

Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 272

An attempt to prepare azidosilane by interaction of azidogermane and fluorosilane exploded.

See related METAL AZIDES, METAL HYDRIDES

†4411. Germane
[7782-65-2] **GeH_4**



ΔH_f° 90 kJ/mol

1. Brauer, 1963, Vol. 1, 715
2. *Chem. Abs.*, 1994, **120**, 80876

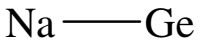
Germane and its higher homologues decompose in air, often igniting [1]. The Japanese have studied the explosive decomposition of germane, the minimum pressure for this was a little more than 0.1 bar [2].

Bromine

See Bromine: Germane

See other METAL HYDRIDES

4412. Sodium germanide
[12265-93-9] **GeNa**



Air, or Water

Johnson, O. H., *Chem. Rev.*, 1952, **51**, 452

The binary alloy is pyrophoric and may ignite in contact with water, as do other alkali metal germanides.

See other ALLOYS, PYROPHORIC MATERIALS

4413. Germanium(II) sulfide

[12025-32-0] **GeS**

$$Ge^{2+(II)} \qquad S^{2-}$$

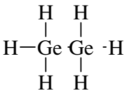
Potassium nitrate

See Potassium nitrate: Metal sulfides

See other METAL SULFIDES

†4414. Digermane

[13818-89-8] **Ge_2H_6**



$H_3Ge{-}GeH_3$

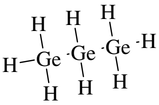
1. Mellor, 1941, Vol. 7, 264
2. Brauer, 1963, Vol. 1, 715
3. McKay, K. M., *Inorg. Synth.*, 1974, **15**, 170

It may ignite in air [1], particularly if air is admitted suddenly into the gas at reduced pressure [2]. Although digermane and its homologues do not usually ignite on exposure to air, their autoignition temperatures appear to be about 50°C and combustion is rapid or explosive [3].

See other METAL HYDRIDES

4415. Trigermane

[14691-44-2] **Ge_3H_8**



Brauer, 1963, Vol. 1, 715

Air-sensitive, it may ignite.

See other METAL HYDRIDES

4416. Poly(dimercuryimmonium hydroxide) (‘Millon’s base anhydride’)

[12529-66-7] **$(HHg_2NO)_n$**

$$Hg{=}\overset{+}{N}{=}Hg \qquad O^{-}H$$

Sidgwick, 1950, 318

The anhydride of Millon’s base explodes if touched or heated to 130°C.

See Mercury: Ammonia

See other FULMINATING METALS, MERCURY COMPOUNDS, N-METAL DERIVATIVES, POLY(DIMERCURYIMMONIUM) COMPOUNDS

4417. Hydriodic acid

[10034-85-2] **HI**

$$H^+ \quad I^-$$

1. Hydrogen iodide is mildly endothermic (ΔH_f° (g) +25.9 kJ/mol, 0.20 kJ/g).
2. Muir, G. D., private comm., 1968

During preparation of hydriodic acid by distillation of phosphorus and wet iodine, the condenser became blocked with by-product phosphonium iodide, and an explosion, possibly also involving phosphine, occurred. There is also a purification hazard.

See Phosphorus: Hydriodic acid

Metals

See Magnesium: Hydrogen halides
Potassium: Hydrogen halides

Oxidants

Leleu, *Cahiers*, 1974, (75), 271

Hydrogen iodide ignites in contact with fluorine, dinitrogen trioxide, dinitrogen tetraoxide and fuming nitric acid.

See Ethyl hydroperoxide: Hydriodic acid
Perchloric acid: Iodides
Potassium chlorate: Hydrogen iodide

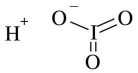
Phosphorus

See Phosphorus: Hydriodic acid

See other INORGANIC ACIDS, NON-METAL HALIDES, NON-METAL HYDRIDES

4418. Iodic acid

[7782-68-5] **HIO_3**



Non-metals

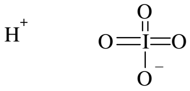
1. Mellor, 1946, Vol. 5, 15
2. Partington, 1967, 813

Interaction with boron below 40°C is vigorous, attaining incandescence [1]. Charcoal, phosphorus and sulfur deflagrate on heating [2].

See other INORGANIC ACIDS, IODINE COMPOUNDS, OXIDANTS, OXOHALOGEN ACIDS

4419. Periodic acid

[13444-71-8] **HIO_4**



Dimethyl sulfoxide

Rowe, J. J. M. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 1924

Although 1.5 M solutions of periodic acid in dimethyl sulfoxide explode after a few min, 0.15 M solutions appear stable.

See Dimethyl sulfoxide: Metal oxosalts, or: Perchloric acid

Tetraethylammonium hydroxide

1. Cookson, R. C. *et al., Chem. Brit.*, 1979, **15**, 329
2. Kirby, G. W. *et al,., J. Chem. Soc., Perkin Trans.*, 1981, 3252

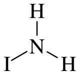
During the preparation of the quaternary oxidant tetraethylammonium iodate from the aqueous reagents, the residue after vacuum evaporation of most of the water exploded, breaking the flask. This was attributed to possible presence of excess periodic acid in the reaction mixture [1]. Further details and precautions to avoid heating the salt, normally stable in storage, are given [2].

See QUATERNARY OXIDANTS

See other INORGANIC ACIDS, IODINE COMPOUNDS, OXIDANTS, OXOHALOGEN ACIDS

4420. Diiodamine (Iodimide)

[15587-44-7] **HI_2N**



Mellor, 1940, Vol. 8, 607

Explosive, formed on prolonged contact of nitrogen triiodide with water.

See NITROGEN TRIIODIDE—AMMONIA

See other N-HALOGEN COMPOUNDS

4421. Potassium hydride

[7693-26-7] **HK**

K^+ H^-

1. Sorbe, 1968, 67
2. Brown, C. A., *J. Org. Chem.*, 1974, **39**, 3913—3918

It ignites on exposure to air [1], and the hydride dispersed in oil is much more highly reactive than sodium hydride dispersions, and rather more careful handling is necessary for safe working. Such precautions are detailed. Contact with water of even traces of the dispersion in flammble solvents will lead to ignition [2].

See Potassium hexahydroaluminate

Bromopentaborane(9), Dimethyl ether

Anon., *Lab. Accid. Higher Educ.*, Item 11, HSE, Barking, 1987

During the reaction of bromopentaborane and potassium hydride in dimethyl ether at —78°C, the reaction became uncontrollable, shattering the glassware and igniting. Cause may have been contamination or effect of scale-up.

O-2,4-Dinitrophenylhydroxylamine

See *O*-2,4-Dinitrophenylhydroxylamine: Potassium hydride

Fluoroalkene (unspecified)

MCA Case History No. 2134

After a few minutes' reflux at 12°C, a mixture of the hydride (0.01 mol) and a fluoroalkene (0.02 mol) exploded violently. This was attributed to possible presence of metallic potassium in the hydride, causing polymerisation or formation of a fluoroacetylene.

Oxidants

See Fluorine: Metal hydrides
Oxygen (Gas): Metal hydrides
See other METAL HYDRIDES

4422. Potassium hydroxide

[1310-58-3] **HKO**

HCS 1980, 768

Acids

MCA Case History No. 920

Incautious addition of acetic acid to a vessel contaminated with potassium hydroxide caused eruption of the acid.
See other NEUTRALISATION INCIDENTS

Ammonium hexachloroplatinate

See Ammonium hexachloroplatinate: Potassium hydroxide

1,4-Bis(1,2-dibromoethyl)benzene

See 1,4-Bis(1,2-dibromoethyl)benzene: Potassium hydroxide

2-Bromo-2,5,5-trimethylcyclopentanone, Triethylamine

See 2-Bromo-2,5,5-trimethylcyclopentanone: Potassium hydroxide, etc.

Bromoform, Cyclic polyethylene oxides

See Bromoform: Cyclic polyethylene oxides, etc.

Chlorine dioxide MRH 1.88/55

See Chlorine dioxide: Potassium hydroxide

Cyclopentadiene

See Cyclopentadiene: Potassium hydroxide

Diamond

See Carbon: Potassium hydroxide

Germanium

Partington, 1967, 181

Germanium is oxidised by the fused hydroxide with incandescence.

Glass

Lloyd, A., *Chem. Brit.*, 1987, **23**, 208

During the distillation of hexane from potassium hydroxide pellets, it was found that the 2 l flask had become perforated by alkaline attack, and that hexane was leaking through two pinholes, generating much flammable vapour. The high rate of corrosion of glass is probably associated with the fact that fresh pellets of potassium hydroxide already contain some 14% of water, and absorption of further water from solvents during drying over potash pellets leads to formation of drops of very concentrated aqueous potassium hydroxide solution.

See other CORROSION INCIDENTS, GLASS INCIDENTS

Glycols

There are no reports of mishap, but:

See Sodium hydroxide: Glycols

Hyponitrous acid

See Hyponitrous acid: Alone, or Potassium hydroxide

Maleic anhydride MRH 1.67/99+

See Maleic anhydride: Bases, etc.

Nitroalkanes MRH Nitromethane 5.69/99+, nitroethane 4.52/99+

See Nitromethane: Acids, etc.

See NITROALKANES: Inorganic bases

Nitroaryl compounds

Solid mixtures may deflagrate readily.

See 4-Chloronitrobenzene: Potassium hydroxide
  Nitrobenzene: Alkali
  4-Nitrobenzoic acid: Potassium hydroxide
  4-Nitrophenol: Potassium hydroxide
  2-Nitrophenol: Potassium hydroxide

See DEFLAGRATION INCIDENTS

Nitrogen trichloride

See Nitrogen trichloride: Initiators

Other reactants

Yoshida, 1980, 212

MRH values calculated for 10 combinations, largely with catalytically decomposed materials, are given.

Potassium peroxodisulfate

See Potassium peroxodisulfate: Potassium hydroxide

Sugars

See SUGARS

2,2,3,3-Tetrafluoropropanol

See 2,2,3,3-Tetrafluoropropanol: Potassium hydroxide

Tetrahydrofuran

See Tetrahydrofuran: Caustic alkalies

Thorium dicarbide

See Thorium dicarbide: Non-metals, etc.

2,4,6-Trinitrotoluene

See 2,4,6-Trinitrotoluene: Added impurities

Water

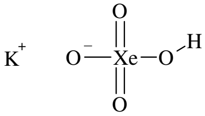
Anon., *CISHC Chem. Safety Summ.*, 1976, **46**, 8—9

A mixture of flake potassium hydroxide and sodium hydroxide was added to a reaction mixture without the agitator running. When this was started the batch erupted, owing to the sudden solution exotherm. Although this is a physical hazard rather than a chemical hazard, similar incidents have occurred frequently.

See Sodium hydroxide: Water.

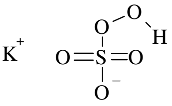
See other AGITATION INCIDENTS, INORGANIC BASES

4423. Potassium hydrogen xenate
[73378-54-8], sesquihydrate **HKO_4Xe**



See other XENON COMPOUNDS

4424. Potassium hydrogen peroxomonosulfate
[10058-23-8] **HKO_5S**



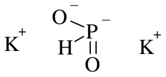
Alone, or Organic matter

Castrantas, 1965, 5

It melts with decomposition at 100°C, and forms explosive mixtures with as little as 1% of organic matter.

See other PEROXOACID SALTS

4425. Dipotassium phosphinate
[13492-26-7] **HK_2O_2P**



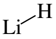
Water

Mellor, 1971, Vol. 8, Suppl. 3, 623

The salt ignites in contact with a little water.

See other METAL PHOSPHINATES, REDUCANTS

4426. Lithium hydride
[60380-67-8] **HLi**



1. Bailar, 1973, Vol. 1, 344
2. Brinza, V. A. *et al., Chem. Abs.*, 1979, **91**, 96308

The powdered material burns readily on exposure to air [1], and the rate of combustion of air suspensions has been studied with respect to concentrations of hydride and moisture in the air [2].

Dinitrogen oxide

See Dinitrogen oxide: Lithium hydride

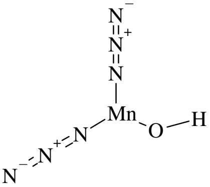
Oxygen

See Oxygen (Gas): Metal hydrides

Oxygen (Liquid): Lithium hydride

See other METAL HYDRIDES

4427. Manganese diazide hydroxide
[ ] **$HMnN_6O$**



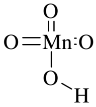
Mellor, 1940, Vol. 8, 354

It explodes at 203°C.

See related METAL AZIDES

4428. Permanganic acid

[13465-41-3] **$HMnO_4$**



Organic materials

1. Frigerio, N. A., *J. Amer. Chem. Soc.*, 1969, **91**, 6201
2. von Schwartz, 1918, 327

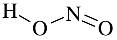
The crystalline acid and its dihydrate are very unstable, often exploding at about 3° and 18°C, respectively, but they may be stored virtually unchanged at —75°C. The anhydrous acid ignited explosively every organic compound with which it came into contact except mono-, di- or tri-chloromethanes [1]. The solution of permanganic acid (or its explosive anhydride, dimanganese heptoxide) produced by interaction of permanganates and sulfuric acid, will explode on contact with benzene, carbon disulfide, diethyl ether, ethanol, flammable gases, petroleum or other organic substances [2].

See Dioxonium hexamanganato(VII)manganate

See other INORGANIC ACIDS, OXIDANTS

4429. Nitrous acid

[7782-77-6] **HNO_2**



A semicarbazone, Silver nitrate

Mitchell, J. J., *Chem. Eng. News*, 1956, **34**, 4704

Use of nitrous acid to liberate a free keto-acid from its semicarbazone caused formation of hydrogen azide which was co-extracted into ether with the product. Addition of silver nitrate to precipitate the silver salt of the acid also precipitated silver azide, which later exploded on scraping from a sintered disc. The possibility of formation of free hydrogen azide from interaction of nitrous acid and hydrazine or hydroxylamine derivatives is stressed.

2-Amino-5-nitrophenol

See 2-Amino-5-nitrophenol: Nitrous acid

Ammonium decahydrodecaborate(2—)

See Ammonium decahydrodecaborate(2—): Nitrous acid

Anilines

Diazonium compounds or solutions produced by action of nitrous acid on the anilines below have been involved in various incidents.

See Aniline, 4-Bromoaniline, 2-Chloroaniline, 3-Chloroaniline, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline.

Phosphine

See Phosphine (reference 3)

Phosphorus trichloride

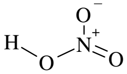
Mellor, 1940, Vol. 8, 1004

The trichloride explodes with nitrous (or nitric) acid.

See other INORGANIC ACIDS, OXIDANTS

4430. Nitric acid

[7697-37-2] **HNO_3**



(*MCA SD-5*, 1961); *FPA H23*, 1974; *HCS 1980*, 678 ($<70\%$), 679 ($>70\%$); *RSC Lab. Hazards Data Sheet No. 32*, 1985

1. *MCA SD-5*, 1961
2. Bretherick, L., *CISHC Chem. Safety Summ.*, 1978, **49**(197), 3
3. Merck, 11th edn., 6497
4. Kirk Othmer, 3rd edn., Vol. 6, 866
5. Editor's comments, 1999

The oxidising power and hazard potential of nitric acid increases progressively with increase in strength from the conc. acid (70 wt%) through fuming acids (above 85 wt%) to the anhydrous 100% acid. Nitric acid is the common chemical most frequently involved in reactive incidents (note the extent of this compound entry), and this is a reflection of its exceptional ability to function as an effective oxidant even when fairly dilute (unlike sulfuric acid) or at ambient temperature (unlike perchloric acid). Its other notable ability to oxidise most organic compounds to gaseous carbon dioxide, coupled with its own reduction to gaseous 'nitrous fumes' has been involved in many of the incidents in which closed, or nearly closed, reaction vessels or storage containers have failed from internal gas pressure [2]. Screw-capped winchesters of fuming acid may therefore develop internal pressure if the inert liner to the plastic cap fails or is missing.

There is a potentially dangerous confusion over the meaning of fuming nitric acid. Once, and sometimes still [3], this meant the red fuming acid which consists of nitrogen dioxide dissolved in nitric acid. This is a potent oxidising agent [1] and best avoided for nitrations, where oxidation is an unwanted and dangerous side-reaction. Increasingly, however, the white fuming acid of American Chemical Society analytical specification [4] is meant. This is a good nitrating agent but a poor oxidant, showing induction periods of hours in length followed by autocatalytic runaway. When following previous literature it is wise to consider which was meant. Nitric acid generally is becoming whiter and less oxidant, which can be partially rectified by adding sodium nitrite.

Anhydrous nitric acid is miscible even with hydrocarbons, and the increased availability of high quality white grades increases the danger of inadvertently forming such mixtures. If anywhere near stoichiometric composition, an homogeneous mixture of nitric acid and virtually any organic is a sensitive high explosive. So much was obvious to learned men of the last century, and many such mixtures were patented as

explosives, by Sprengel and others, from 1871 onwards. Correspondence makes it apparent that this property is neither known nor obvious to all Professors of Chemistry in the late 1990s: though learning has departed, danger has not [5]!
See Polyalkenes, below
See other GAS EVOLUTION INCIDENTS

Acetic acid

1. Raikova, V. M., *Chem. Abs.*, 1983, **98**, 5958
2. Vidal. P. *et al., C. R. Acad. Sci. Ser. II*, 1991, **313**(12), 1383; *J. Energ. Mater.*, 1993, **11**(21), 135.

Critical detonation diameters for mixtures have been determined.

Acetic acid, Sodium hexahydroxyplatinate(IV)

1. Davidson, J. M. *et al., Chem. & Ind.*, 1966, 306
2. Malerbi, B. W., *Chem. & Ind.*, 1970, 796

During preparation of diacetatoplatinum(II) by alternative procedures, the hexahydroxyplatinate in mixed nitric—acetic acids was evaporated to a syrup and several explosions were experienced [1], possibly owing to formation of acetyl nitrate. On one occasion a brown solid was isolated and dried, but subsequently exploded with great violence when touched with a glass rod. The material was thought to be a mixture of platinum (IV) acetate—nitrate species [2].

Acetic anhydride MRH 4.94/34

1. Brown, T. A. *et al., Chem. Brit.*, 1967, **3**, 504
2. Dubar, J. *et al., Compt. rend. C*, 1968, **266**, 1114
3. Dingle, L. E. *et al., Chem. Brit.*, 1968, **4**, 136
4. Ullmann, A10, 157
5. *MCA Case History No. 103*
6. Venters, K. *et al., Chem. Abs.*, 1982, **97**, 45372
7. Raikova, V. M., *Chem. Abs.*, 1983, **98**, 5958
8. Andreozzi, R. *et al., J. Haz. Mat.*, 2002, **90**(2), 111

Mixtures containing 50—85 wt% of fuming nitric acid are detonable and very sensitive to initiation by friction or shock (possibly owing to formation of acetyl nitrate and/or tetranitromethane). For preparation of mixtures outside these limits, the order of mixing is important (below 50%, acid into anhydride; above 85%, vice versa; and all below 10°C) [1]. Similar information is also presented diagrammatically [2]. Mixtures containing less than 50% of nitric acid are also dangerous in that addition of small amounts of water (or water-containing mineral acids) readily initiates an uncontrollable exothermic fume-off, which will evaporate most of the liquid present. Equimolar mixtures of 38% nitric acid with acetic anhydride can be detonated at room temperature after aging for a few h [3]. Others put the lower limit of detonability at 30% [4]. Accidental contact of the 2 materials caused a violent explosion [5]. Thermodynamic calculations show maximum values for heats of decomposition for acetyl nitrate or its equivalent mixtures of the components [6]. Critical detonation diameters for mixtures have been determined [7]. Calorimetric studies of mixtures of varied composition is reported and modelled [8].
See 1,3,5-Triacetylhexahydrotriazine, etc., below

Acetic anhydride, Hexamethylenetetramine acetate

Leach, J. T., *J. Haz. Mat.*, 1981, **4**, 271—281

The military explosives RDX and HMX are manufactured from the 3 components using the Bachman process. Some of the possible mixtures may lead to fires in open vessels and explosions under confinement, and the exothermic and other effects (some calculated by the CHETAH program) for a wide range of mixtures are presented as ternary diagrams. It was also found that acetic anhydride layered onto solutions of ammonium nitrate in nitric acid exploded, owing to formation of acetyl nitrate.

Acetone MRH 5.86/23

1. Kennedy, R., private comm., 1975
2. Anon., *Safety Digest Univ. Safety Assoc.*, 1989, **34**, 14

A winchester of fuming nitric acid with a plastics cap burst, probably owing to internal pressure build-up and uneven wall thickness. The explosion fractured an adjacent bottle of acetone which ignited on contact with the oxidant [1]. Segregation of oxidants and fuels in storage is essential to prevent such incidents, which have occurred previously elsewhere. Another explosion resulted, when attempting to clear a jammed glass stopper by successive application of acetone and nitric acid [2].

See Polyalkenes, below,

See also SAFE STORAGE OF CHEMICALS

Acetone, Acetic acid

1. Frant, M. S., *Chem. Eng. News*, 1960, **38**(43), 56
2. Secunda, W. J., *Chem. Eng. News*, 1960, **38**(46), 5

A mixture of equal parts of nitric acid, acetone and 75% acetic acid, used to etch nickel, will explode 1.5—6 h after mixing if kept in a closed bottle. The presence of the diluted acetic acid would probably slow the known violent oxidation of acetone by nitric acid [1] (but would not prevent slow oxidation with gas evolution). Alternatively, the formation of tetranitromethane and subsequent oxidation of acetone was postulated [2], but this is perhaps unlikely, because presence of acetic anhydride is normally necessary for formation of tetranitromethane.

Acetone, Sulfuric acid

Fawcett, H. H., *Ind. Eng. Chem.*, 1959, **51**, 89A

Acetone is oxidised violently by mixed nitric—sulfuric acids, and if the mixture is confined in a narrow-mouthed vessel, it may be ejected or explode.

Acetonitrile MRH 6.15/23

Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542

Mixtures of fuming nitric acid and acetonitrile are high explosives.

4-Acetoxy-3-methoxybenzaldehyde

Legrand, M. *et al., J. Chem. Educ.*, 1978, **55**, 769

The dangerously exothermic nitration of the aldehyde with conc. nitric acid is adequately controlled on a several hundred g scale by an automated assembly of laboratory apparatus.

Acetylene, Mercury(II) salts, Sulfuric acid

Orton, K. J. P. *et al., J. Chem. Soc.*, 1920, **117**, 29

Contact of acetylene with the conc. acid in presence of mercury salts forms trinitromethane, explosive above its m.p., 15°C. Subsequent addition of sulfuric acid produces tetranitromethane, a powerful oxidant of limited stability, in high yield.

See Trinitromethane

See also Tetranitromethane

Acrylonitrile

See Acrylonitrile: Acids

Acrylonitrile—methacrylate copolymer

Caprio, V. *et al., J. Haz. Mat.*, 1983, **7**, 383—391

The Asahi process for wet-spinning the copolymer involves water dilution at below 0°C of a solution of the copolymer in aqueous 68 wt% nitric acid (the azeotropic composition). The potential for slow self heating and decomposition have been investigated experimentally with variations in several parameters in a Sikarex safety calorimeter. At 20% polymer content, the slow self heating starts even at ambient temperature, and later involves evolution of 30 mol of uncondensable gas per kg of copolymer with comcommittant boiling of the nitric acid. A 2 step mechanism has been proposed.

See other GAS EVOLUTION INCIDENTS

Alcohols MRH Ethanol 5.56/24, furfuryl alcohol 5.86/28

1. Fawcett, H. H., *Chem. Eng. News*, 1949, **27**, 1396
2. Fromm, F. *et al.*, *Chem. Eng. News*, 1949, **27**, 1956
3. Unpublished observations, 1956
4. *MCA Case History No. 1152*
5. Potter, C. R., *Chem. & Ind.*, 1971, 501
6. Spengler, G. *et al., Brennst. Chem.*, 1965, **46**, 117
7. Long, L. A., private comm., 1972
8. Kurbangalina, R. K., *Zh. Prikl. Khim.*, 1959, **32**, 1467—1470
9. Albright, Hanson, 1976, 341—343
10. Anon., *CIHSC Chem. Safety Summ.*, 1980, **51**, 4
11. Anon., *Loss Prev. Bull.*, 1980, (035), 7—9
12. Anon., *Univ. Safety Assoc. Safety News*, 1982, (16), 4
13. Mabbott, D. J., 1996, personal communication
14. Westerterp, K. R. et al., *Chem. Engng. Processing*, 2002, **41**(1), 59
15. Ceru, B., *Safe Science (Michigan State University)*, 1993, Sept, 1

A 15% solution of nitric acid in ethanol was used to etch a bismuth crystal. After removing the metal, the mixture decomposed vigorously [1]. Mixtures of nitric acid and alcohols ('Nital') are quite unstable when the concentration of acid is above 10%, and mixtures containing over 5% should not be stored [2]. The use of a little alcohol and excess nitric acid to clean sintered glassware (by 'nitric acid fizzing') is not recommended. At best it is a completely unpredictable approximation to a nitric acid—alcohol rocket propulsion system. At worst, if heavy metals are present, fulminates capable of detonating the mixture may be formed [3]. Chromic acid mixture is less hazardous for such cleaning operations. The Case History describes a violent explosion caused by addition of conc. Acid to a tank car contaminated with a little ethanol [4]. During oxidation of cyclohexanol to the 1,2-dione by an established process, a violent explosion occurred. Two intermediates are possible suspects [5]. Furfuryl alcohol is hypergolic with high-strength nitric acid [6] and methanol has been used as a propellant fuel. It also readily forms the explosive ester, methyl nitrate [7]. Mixtures with ethylene glycol are easily detonated by heat, impact or friction [8]. The injector process for safe continuous nitration of glycerol and other alcohols is reviewed [9]. Use of the wrong proportions of denatured ethanol and nitric acid (5:95 instead of 95:5) led to an explosion [10]. During attempts to clean a reactor, unclear instructions led to 120 l of conc. Nitric acid, rather than the aqueous 2.6% solution intended, being charged via a pump which contained some 5 l of 2-propanol from previous use. Rapid oxidation of the alcohol, (probably accompanied by formation of explosive isopropyl nitrate) and gas evolution burst the reactor [11]. A stock solution of conc. Nitric acid in methanol for cleaning glassware was stored in a screw-capped bottle which later burst from internal gas pressure. Such mixtures are dangerously unstable and should not be used or stored [12]. A 33% by volume solution of nitric acid in ethanol was mixed for metallurgical purposes in a large open bottle, after two hours the still warm mixture was capped. Perhaps 7 hours after mixing, there was an exceedingly violent explosion. It was decided not to use this mixture in future but to substitute one containing perchloric acid, (which may be no less hazardous) [13]. A mixture with 2-propanol was deliberately prepared for an unstated end. Reaction started shortly aftermwards ledaing to an explosion as an attempt was made to loosen the cap on the hissing bottle [15]. An extensive study of safe procedure for oxidation of secondary alcohols to ketones, using 2-octanol as the model substrate, has been published [14].

See Methanol, Sulfuric acid, below

See other GAS EVOLUTION INCIDENTS, NITRATION INCIDENTS, PLANT CLEANING INCIDENTS

Alcohols, Disulfuric acid

Rastogi, R. P. *et al., Amer. Inst. Aero. Astronaut. J.*, 1966, **4**, 1083—1085

Ignition delays were determined for contact of various aliphatic alcohols with mixtures of disulfuric acid (*d*, 1.9) and red fuming nitric acid (*d*, 1.5). With ethanol, a minimum of 30 wt% of disulfuric acid was required for ignition.

Alcohols, Potassium permanganate

See Potassium permanganate: Alcohols, Nitric acid

Aliphatic amines

1. Schalla, R. L. *et al., Amer. Rocket Soc. J.*, 1959, **29**, 33—39
2. Schneebeli, P. *et al., Rech. Aeron.*, 1962, **87**, 33—46

In contact with white fuming nitric acid, ignition delays for tributylamine, tripropylamine and triethylamine were less than those of the corresponding dialkylamines, and under good mixing conditions, butylamine did not ignite [1]. Triethylamine ignites on contact with the conc. acid [2].

See Aromatic amines (reference 2); Cyclohexylamine; and Dinitrogen tetraoxide: Nitrogenous fuels, all below

Alkanethiols

1. Filby, W. G., *Lab. Practice*, 1974, **23**, 355
2. McCullough, F. *et al., Proc. 5th Comb. Symp.*, 181, New York, Reinhold, 1955
3. Illingworth, B., private comm., 1980
4. Quam, G. N., *Safety Practice for Chemical Laboratories*, 52—53, Villanova (Pa.), Villanova Press, 1963
5. Reychler, A., *Bull. Soc. Chim. Belg.*, 1913, **110**, 217, 300

Oxidation of alkanethiols to alkanesulfonic acids with excess conc. acid as usually described is potentially hazardous, the exotherm often causing ignition of the thiol. A modified method involving oxidation under nitrogen and at temperatures 1—2°C above the m.p. of the thiol is safer and gives purer products [1]. Technical butanethiol (containing 28% of propane- and 7% of pentane-thiols) is hypergolic with 96% acid [2]. Oxidation of several thiols to the sulfonic acids by addition to stirred conc. acid had been effected normally, but when 2 new batches of pentanethiol were used, flame was observed in the vapour phase a few s after addition. No unusual impurities were detected. The oxidation can be effected safely with nitric acid—water (2:3) with rapid stirring at below 35°C [3]. Oxidation of dodecanethiol [4] and hexadecanethiol [5] with fuming nitric acid proceeded explosively.

2-Alkoxy-1,3-dithia-2-phospholane (‘O-Alkyl ethylene dithiophosphate’)

Arbuzov, A. E. *et al., Chem. Abs.*, 1953, **47**, 4833e,f

The methoxy and ethoxy derivatives ignite with the conc. acid.

See Phosphorus compounds, below

Alkylamines

1. Vouillamox, L., *Chimia*, 1995, **49**(11), 439

During propionitrile manufacture by oxidative amination of propanol, nitric acid was used for neutralisation. This eventually led to concentration of nitrates, which exploded, at the bottom of the final distillation column [1]. Many amines form highly crystalline nitrates, which are usually explosive once isolated.

See AMINIUM NITRATES

2-Aminothiazole

Biasutti, G. S. *et al., Loss. Prev.*, 1974, **8**, 123—125

In an attempt to produce the nitrate salt, 2-aminothiazole was added to the required amount of nitric acid and the mixture stirred and heated: the mixture exploded without warning.

See other NITRATION INCIDENTS

2-Aminothiazole, Sulfuric acid

Silver, L., *Chem. Eng. Progr.*, 1967, **63**(8), 43

Nitration of 2-aminothiazole with nitric—sulfuric acids was normally effected by mixing the reactants at low temperature, heating to 90°C during 30 min and then applying cooling. When the cooling was omitted, a violent explosion occurred.

Experiment showed that this was due to a slow exothermic reaction accelerating out of control under the adiabatic conditions. *N*-Nitroamines were not involved.
See other NITRATION INCIDENTS, SELF-ACCELERATING REACTIONS

Ammonia
Mellor, 1940, Vol. 8, 219
A jet of ammonia will ignite in nitric acid vapour.

Ammonium nitrate
Biasutti, 1981, 135
Decomposition of a 70% nitric acid—ammonium nitrate slurry explosive led to overflow, contact with wood and a fire. (Any explosive formulation must also have included a fuel). This spread to detonators, which initiated detonation of the slurry.

Anilinium nitrate
Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542
Although aniline may be hypergolic with nitric acid (below), anilinium nitrate dissolves unchanged in 98% acid and can be stored for long periods, though the solution has explosive properties.
See Cyclohexylamine, below

Anilinium nitrate, Inorganic additives
Munjal, M. N. *et al., Indian J. Chem.*, 1967, **5**, 320—322
The effect of inorganic additives upon ignition delay in anilinium nitrate—red fuming nitric acid systems was examined. The insoluble compounds copper(I) chloride, potassium permanganate, sodium pentacyanonitrosylferrate and vanadium(V) oxide were moderately effective promoters, while the soluble ammonium or sodium metavanadates were very effective, producing vigorous ignition.

Aromatic amines MRH Aniline 5.98/19

1. Kit and Evered, 1960, 239, 242
2. *Aniline*, 85, Allied Chem. Corp., New York, 1964
3. Miller, R. O., *Tech. Note No. 3884*, 1—32, Washington, Nat. Advisory Comm. Aeronaut., 1956
4. Spengler, G. *et al., Brennst. Chem.*, 1965, **46**, 1172
5. Bernard, M. L. *et al., Compt. rend. C*, 1966, **263**, 24—26
6. Schalla, R. L. *et al., Amer. Rocket Soc. J.*, 1959, **29**, 38

Many aromatic amines (aniline, *N*-ethylaniline, *o*-toluidine, xylidine, etc., and their mixtures) are hypergolic with red fuming nitric acid [1]. When the amines are dissolved in triethylamine, ignition occurs at —60°C and below [2]. Addition of a mixture of aniline, dimethylaniline, xylidine and pentacarbonyliron renders hydrocarbons hypergolic with conc. nitric acid [3]. Although aniline is not hypergolic with 96% acid, presence of sulfuric acid (5% or above) renders it so. Presence of dinitrogen tetraoxide further reduces ignition delay [4]. The mechanism of ignition of *p*-phenylenediamine (or furaldehyde azine) on contact with red fuming nitric acid is quantified [5]. Traces of sulfuric acid may be essential for ignition to occur [6].
See Benzidine, below

Aromatic amines, Metal compounds

Rastogi, R. P. *et al., Indian J. Chem.*, 1964, **2**, 301—307

The effects of various metal oxides and salts which promote ignition of amine—red fuming nitric acid systems were examined. Among soluble catalysts, copper(I) oxide, ammonium metavanadate, sodium metavanadate, iron(III) chloride (and potassium hexacyanoferrate(II) with *o*-toluidine) are most effective. Of the insoluble materials, copper(II) oxide, iron(III) oxide, vanadium(V) oxide, potassium chromate, potassium dichromate, potassium hexacyanoferrate(III) and sodium pentacyanonitrosylferrate(II) were effective.

See Anilinium nitrate, etc.

See also Aromatic amines (reference 3), above

Aromatic compound

Anon., *Safety Digest Univ. Safety Assoc.*, 1989, **34,** 13

An explosion resulted on nitrating an unrevealed aromatic, possibly a phenethyl alcohol derivative, with fuming nitric at —40°C, adding the acid to substrate. Probably too cold and too basic for initial reaction, leading to runaway (oxidation?) when almost all the nitric acid had been charged. Nitration only proceeds when the acidity is sufficient to protonate much of the nitric acid present, in this context any oxygen in the substrate is a base. The editor's experience is that, for monoalkylbenzenes, nitration is very slow, even with substantial sulfuric acid also present as catalyst and dehydrating agent, at —20°C and below. Red fuming nitric acid, which contains dissolved oxides, encourages oxidation (much more exothermic, autocatalytic and gas evolving) in place of nitration.

See Benzeneethanol, below

See other NITRATION INCIDENTS

Arsine—boron tribromide

See Arsine—boron tribromide: Oxidants

Benzeneethanol, Sulfuric acid

Rashevskaya, S. K. *et al., Zh. Obshch. Khim., 1963,* **33**(12), 3998; *Chem. Abs.*, 1964, 9178f

Indifferent yields of mononitro-products resulted from nitration in 1:1 nitric and sulfuric acid at 0°C. At 18°C there was an explosion. (The editor has dinitrated this compound with no trouble, but he used far more sulfuric acid and added the nitric acid to the other components).

See 2-Methoxyethylbenzene, Sulfuric acid; below

See other NITRATION INCIDENTS

Benzidine

Krishna, P. M. M. *et al., Chem. Abs.*, 1981, **94**, 124107

Benzidine is hypergolic with red fuming nitric acid.

See Aromatic amines, above

Benzo[*b*]thiophene derivatives

Brown, I. *et al., Chem. & Ind.*, 1962, 982

During nitration of several amino derivatives, diazotisation and oxidation occurred to produce internal diazonium phenoxide compounds. 5-Acetylamino-3-bromobenzo[*b*]thiophene unexpectedly underwent hydrolysis, diazotisation and oxidation to the explosive compound below.
See 3-Bromo-2,7-dinitro-5-benzo[*b*]thiophenediazonium-4-oxide
See 4-Chloro-2-nitroaniline, below
See other NITRATION INCIDENTS, PLANT CLEANING INCIDENTS

Benzonitrile, Sulfuric acid
Anon., *Loss. Prev. Bull.*, 1978, (024), 168
Nitration of benzonitrile by addition to mixed nitrating acid had been effected uneventfully in 250 batches. Plant 'improvements' led to the same dosing vessel being used alternately for the nitrile and mixed acids. Some nitration occurred in the uncooled and unstirred dosing vessel containing a little residual nitrile and an explosion occurred during the second batch in the modified plant.

N-Benzyl-*N*-ethylaniline, Sulfuric acid
Anon., *Loss. Prev. Bull.*, 1978, (024), 169; 1980, (038), 27
Addition of 2—3 l of the amine to a dosing vessel not completely free of traces of mixed acids led to a vigorous decomposition which burst a vent line.
See other NITRATION INCIDENTS, PLANT CLEANING INCIDENTS

1,4-Bis(methoxymethyl)2,3,5,6-tetramethylbenzene
Anon., *Jahresber.*, 1972, 84
Oxidation of the durene derivative to benzenehexacarboxylic acid (mellitic acid) in an autoclave is normally effected in stages, initially by heating at 80—104°C with the vent open to allow escape of the evolved gases. Subsequent heating to a higher temperature with the vent closed completes the reaction. On one occasion omission of the first vented heating phase led to explosive rupture of the autoclave at 80°C.
See Hydrocarbons, below
See other GAS EVOLUTION INCIDENTS

1,3-Bis(trifluoromethyl)benzene, Sulfuric acid
Grewer, T., *Proc. 1st Int. Symp. Prev. Occ. Risks in Chem. Ind.*, 153—160, Heidelberg, ISSA, 1970
The fluoro compound is resistant to nitration and an operating temperature of 90°C is necessary to ensure formation of the 5-nitro derivative. Under these conditions, the atmosphere (containing the fluoro compound, its nitro derivative and nitric acid vapours) in the nitration vessel is explosive and above the flash point. An unknown ignition source led to an explosion and rupture of the 3 cu. m vessel, and a maximum explosion pressure of 50 bar was confirmed experimentally. Such explosive atmospheres are not found in low temperature nitration reactions.
See Chlorobenzene, below
See other NITRATION INCIDENTS

Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.

tert-Butyl-*m*-xylene, Sulfuric acid

Kotoyori, T., private comm., 1983

Normally, the hydrocarbon (360 kg) was tri-nitrated by slow addition during 15 h to premixed 97% nitric—98% sulfuric acids (wt ratio 1.04:1, 1470 kg) agitated at 35—40°C, maintaining the temperature (checked at 30 min intervals) by controlling the jacket cooling and rate of addition. Because of a confusing and inadequate control panel layout, stirring was accidentally stopped after 3.3 h and addition was continued for a further 2 h before the absence of agitation was noticed, when the temperature was 34°C, and addition was stopped. At this stage, a layer of the liquid hydrocarbon (45 kg, $d = 0.8$) would be on top of the solid trinitro compound (150 kg, m.p. 112°C), itself floating on the mixed acid (d about 1.75). As the operator realised it would cause an immediate violent exotherm if full agitation were restored, he attempted to start mild agitation by flicking the agitator on for 1 s only. After some 20 s, yellow-brown fumes began to escape from the vent pipe, indicating the onset of exothermic decomposition, so he went to open the dump valve but was prevented by the thick fumes. During the next couple of minutes the velocity of the fumes (now white) and the associated noise increased to a very high level and the vessel finally exploded, the lid being blown off and the contents becoming ignited.

See other AGITATION INCIDENTS, NITRATION INCIDENTS

Cadmium phosphide

Juza, R. *et al., Z. Anorg. Chem.*, 1956, **283**, 230

Reaction with conc. acid is explosive.

Cellulose

MCA SD-5, 1961

Cellulose may be converted to the highly flammable nitrate ester on contact with the vapour of nitric acid, as well as by the liquid acid.

4-Chloro-2-nitroaniline

1. Elderfield, R. C. *et al., J. Org. Chem.*, 1946, **11**, 820
2. *MCA Case History No. 1489*

The literature procedure for preparation of 4-chloro-2,6-dinitroaniline [1], involving direct nitration in 65% nitric acid, was modified by increasing the reaction temperature to 60°C 1 h after holding at 30—35°C as originally specified. This procedure was satisfactory on the bench scale, and was then scaled up into a 900 l reactor. After the temperature had reached 30°C, heating was discontinued, but the temperature continued to rise to 100—110°C. Decomposition set in with copious evolution of nitrous fumes and production of a very shock-sensitive explosive solid. This was identified as 4-chloro-2,5-dinitrobenzenediazonium-6-oxide, produced by hydrolysis of a nitro group in the expected product by the diluted nitric acid at high temperature, diazotisation of the free amino group by the nitrous acid produced in the hydrolysis (or by the nitrous fumes), and introduction of a further nitro group under the prevailing reaction conditions. It is recommended that primary aromatic amines should be protected by acetylation before nitration, to prevent the possibility of accidental diazotisation.

See Benzo[*b*]thiophene derivatives, above,

See also ARENEDIAZONIUM OXIDES
See other NITRATION INCIDENTS

Chlorobenzene

Anon., *Jahresber.*, 1974, 86

In a plant for the continuous nitration of chlorobenzene, maloperation during start-up caused the addition of substantial amounts of reactants into the reactor before effective agitation and mixing had been established. The normal reaction temperature of 60°C was rapidly exceeded by at least 60° and an explosion occurred. Subsequent investigation showed that at 80°C an explosive atmosphere was formed above the reaction mixture, and that the adiabatic vapour-phase nitration would attain a temperature of 700°C and ignite the explosive atmosphere in the reactor.

See 1,3-Bis(trifluoromethyl)benzene, above

See other AGITATION INCIDENTS, NITRATION INCIDENTS, SELF-HEATING AND IGNITION INCIDENTS

Coal

Green, J. B. *et al., Anal. Chem.*, 1979, **51**, 1126

The mixtures of bituminous coal and conc. nitric acid used to prepare nitrohumic acids are potentially explosive, and appropriate care is necessary.

See Organic materials, below

Contaminants

NSC Safety Newsletter, Chem. Sect., July, 1977

A 50% nitric acid solution was used to clean glass containers and then stored in a screw-capped bottle. Some time later the bottle burst, owing to gas generation by the dissolved contaminant(s).

See other GAS EVOLUTION INCIDENTS

Copper

1. Anon., *Loss Prev. Bull.*, 1987, (074), 23—27
2. Anon., *Loss Prev. Bull.*, 1988, (080), 31—34

A ‘canned’ electric pump was being used to pump 89% nitric acid during a plant malfunction when a violent explosion occurred. This was attributed to penetration of nitric acid into the sealed copper windings of the motor and subsequent generation of nitric oxide which pressurised the stator enclosure to some 60—280 bar, causing it to burst. Preventive precautions are detailed [1]. The pump manufacturers, however, subsequently challenged this account and explanation and revealed that the pump, which had been returned for service and repair on previous occasions, had shown signs of reverse rotation and presence of nitric acid in the windings. Such pressure build-up was most unlikely, since the stator enclosure had both an external vent and a separate pressure relief valve. The remains of the exploded pump also showed signs of reverse rotation and the impellor appeared to have come loose on the shaft prior to the explosion. The latter occurred when the motor was energised via replacement fuses

50% above recommended capacity. The precise cause of the explosion is not clear, but may well have been spark-initiated [2].
See IGNITION SOURCES
See other GAS EVOLUTION INCIDENTS

Copper(I) nitride
Mellor, 1940, Vol. 8, 100
Interaction with conc. acid is very violent.

Cotton, Rubber, Sulfuric acid, Water
Biasutti, 1981, 76
A rubber glove and a box of cotton waste fell into a tank of spent nitrating acid from the preparation of TNT. The total contents of the tank ignited, leading to a series of explosions which caused severe damage and some 900 casualties, including 82 killed.
See other NITRATION INCIDENTS

Crotonaldehyde
Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542
Crotonaldehyde is hypergolic with conc. nitric acid, ignition delay being 1 ms.
See ROCKET PROPELLANTS

Cycloalkanones
1. Dye, W. T., *Chem. Eng. News*, 1959, **37**, 48
2. Field, K. W. *et al., J. Chem. Educ.*, 1985, **62**, 637

Oxidation of 4-methylcyclohexanone by addition of nitric acid at about 75°C caused a detonation to occur. These conditions had been used previously to oxidise the corresponding alcohol, but although the ketone is apparently an intermediate in oxidation of the alcohol, the former requires a much higher temperature to start and maintain the reaction. An OTS report, PB73591, mentions a similar violent reaction with cyclohexanone [1]. Presence of nitrous acid is essential for the smooth oxidation of cycloalkanones with nitric acid to α,ω-hexanedioic acids. Because high-purity nitric acid (free of nitrous acid) is now commonly available, addition of a little sodium or potassium nitrite to the acid is necessary before its use to oxidise cycloalkanones [2].
See Acetone, etc., above

Cyclohexanol, Cyclohexanone
1. Wilson, B. J. et al., *Loss. Prev.*, 1979, **12**, 27—29
2. Vidal, P. *et al., Thermochim. Acta*, 1993, **225**(2), 223

The process for manufacturing adipic acid by nitric acid oxidation of KA (the ketone—alcohol mixture produced by air oxidation of cyclohexane in the liquid phase) at 68°C is potentially hazardous, in that reactor or cooling failure could lead to a large and vigorous evolution of hot toxic nitrous fumes. The overall process has been studied and modified to reduce these potential hazards [1]. Solutions of organic diacids in nitric acid, such as result in adipic acid manufacture, were studied for exotherm, gas evolution, deflagration and detonation. Critical diameters were plotted against composition. Recommendations for plant design result [2].

Cyclohexylamine MRH 6.07/18

Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542

Although cyclohexylamine has been used as a fuel with nitric acid in rocket motors, cyclohexylammonium nitrate dissolves unchanged in fuming nitric acid to give a solution stable for long periods.

See Anilinium nitrate, above,

See ROCKET PROPELLANTS

Di-2-butoxyethyl ether

Hanson, C. *et al., Proc. Int. Solvent Extr. Conf.* (Liege), 1980, 2, paper 80—70

The solvent (‘Butex’), an extractant in nuclear reprocessing may decompose violently in contact with nitric acid. Hydrolysis to butanol, followed by violent oxidation, catalysed by nitrous acid, is involved.

See Alcohols, above

1,3-Diacetoxybenzene

See 4,6-Dinitro-1,3-benzenediol

See other INDUCTION PERIOD INCIDENTS, NITRATION INCIDENTS

1,2-Diaminoethanebis(trimethylgold)

See 1,2-Diaminoethanebis(trimethylgold)

1,2-Dichloroethane

Kurbangalina, R. K., *Zh. Prikl. Khim.*, 1959, **32**, 1467

Mixtures are easily detonated by heat, impact or friction.

Dichloroethylene

Raikova, V. M., *Chem. Abs.*, 1983, **98**, 5958

Critical detonation diameters for mixtures have been determined.

Dichloromethane

Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542

Dichloromethane dissolves endothermically in conc. nitric acid to give a detonable solution.

Dichromates, Organic fuels

Munjal, N. L. *et al., Amer. Inst. Aero. Astronaut. J.*, 1972, **10**, 1722—1723

The effects of dichromates in promoting ignition of non-hypergolic mixtures of red fuming nitric acid with cyclohexanol, 2-cresol or 3-cresol, and furfural were studied. Ammonium dichromate was most effective in all cases, and the only effective catalyst for cyclohexanol. Potassium chromate and potassium dichromate were also examined.

Diethyl ether MRH 5.94/21

1. Foote, C. S., private comm., 1965
2. Holt, C., *School. Sci. Rev.*, 1976, **58**(202), 159—160
3. Fischer, E., *Ber.*, 1902, **35**, 3794
4. Anon., *Sichere Chemiearb.*, 1981, **33**, 94—95
5. Anon., *Univ. Saf. Assoc., Saf. Digest*, 1988, (25), 6—8

Addition of ether to a nitration mixture (2-bromotoluene and conc. nitric acid) diluted with an equal volume of water in a separating funnel led to a low order explosion. This was attributed to oxidation of the ether (possibly containing alcohol) by the acid. Addition of more water before adding ether was recommended [1]. Attention is drawn to the delayed vigorous decomposition reaction which occurs some time after the initially homogeneous mixture of conc. nitric acid and ether has separated into 2 phases (possibly involving formation of ethyl nitrate?) [2]. In the preparation of 3-chlorolactic acid by oxidation of epichlorhydrin with nitric acid [3], the product was extracted into ether. Vacuum evaporation of solvent at 40°C led to a violent explosion, wrongly attributed to formation of peroxides. Experiment showed that extraction of 200 ml of a 30% aqueous solution of nitric acid with 8 x 200 ml portions of ether extracted 88% of the acid into the ether [4]. Upon concentration, this would produce very concentrated warm acid in contact with organic material, which would be oxidised violently or explosively (and could form ethyl nitrate). It is dangerous to extract nitric acid solutions with ether or other organic solvents without first removing the excess acid, either by neutralisation or ion exchange.

Nitric acid was being used to clean laboratory glassware to a very high state of surface cleanliness by soaking in a bucket of conc. acid for a week. During this time, one of the empty winchesters was inadvertently used as a solvent residues bottle and some 250 ml of diethyl ether was put in. The acid was to be recovered for re-use and it was put back into the original bottles. When the bottle containing ether was refilled and screw capped, after a few seconds it exploded violently [5].

See Glassware, below

Diethyl ether, Sulfuric acid

1. Kirk-Othmer, 1965, Vol. 8, 479
2. Van Alphen, J., *Rec. Trav. Chim.*, 1930, 492—500

Interaction of ether with anhydrous nitric acid to produce ethyl nitrate may proceed explosively [1], and in presence of conc. sulfuric acid, ether and conc. nitric acid explode violently [2].

See Dimethyl ether, below

Diethylaminoethanol

See 2-Diethylammonioethyl nitrate nitrate

3,6-Dihydro-1,2,2*H*-oxazine

Wichterle, O. *et al., Coll. Czech. Chem. Comm.*, 1950, **15**, 309—321

The product of interaction (possibly an *N*-nitro and/or ring-opened nitrate ester derivative) is explosive.

Dimethyl 4-acetamidophthalate

See Dimethyl 4-acetamidophthalate: Nitric acid

Dimethyl ether

Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542—545

The latent hazards in storing and handling the explosive mixtures with the conc. acid are discussed (methyl nitrate may be formed).

See Diethyl ether, above

Dimethyl sulfide, 1,4-Dioxane

Rudakov, E. S. *et al., Chem. Abs.*, 1972, **76**, 13515

The mechanism which leads to delayed explosion in the system with nitric acid, even when cooled in liquid nitrogen, was investigated.

Dimethyl sulfoxide, Water

Fiola, J. *et al.*, Czech. Pat. 170 169, 1977

During the oxidation of the sulfoxide to the sulfone, the concentration of water in the reaction mixture must be maintained above 14% to prevent the risk of detonation.

Dimethylaminomethylferrocene, Water

Koch-Light Ltd., private comm., 1976

In an assay procedure the amine was heated with diluted nitric acid, and near-explosive decomposition occurred.

1,1-Dimethylhydrazine

See Hydrazine and derivatives, below

1,1-Dimethylhydrazine, Organic compounds

Spengler, G. *et al., Brennst. Chem.*, 1965, **46**, 117

Contact of nitric acid (or dinitrogen tetraoxide) with dimethylhydrazine is hypergolic and well described in rocket technology. While hydrocarbons and several other classes of organic compounds are not hypergolic with these oxidisers, addition of a proportion of dimethylhydrazine to a wide range of hydrocarbons, alcohols, amines, esters and heterocyclic compounds renders them hypergolic in contact with nitric acid or dinitrogen tetraoxide.

1,3-Dinitrobenzene MRH 5.02/99+

Biasutti, 1981, 92

After a detonation during manufacture of an explosive solution of the nitro compound in conc. nitric acid, manufacture was discontinued as being too dangerous.

Dinitrogen tetraoxide, Nitrogenous fuels

1. Durgapal, U. C. *et al., Amer. Inst. Aero. Astronaut. J.*, 1974, **12**, 1611
2. Munjal, N. L. *et al., J. Spacecr. Rockets*, 1974, **11**, 4286—430
3. Durgapal, U. C. *et al., J. Spacecr. Rockets*, 1974, **11**, 447—448

The effect on decrease in hypergolic ignition delay of increasing concentrations of dinitrogen tetraoxide in red fuming nitric acid was studied with triethylamine, dimethylhydrazine or*mixo*-xylidine as fuels [1]. The effect of various catalysts on ignition delay after contact of red fuming nitric acid with various arylamine—formaldehyde condensation products was also studied [2,3].

Dioxane, Perchloric acid

See Perchloric acid: Dioxane, Nitric acid

Diphenyldistibene

See Diphenyldistibene: Air, etc.

Diphenylmercury

Whitmore, 1921, 43, 168

Interaction in carbon disulfide, even at —15°C, is violent.

Diphenyltin

Krause, E. *et al., Ber.*, 1920, **53**, 177

Ignition occurs on contact with fuming nitric acid.

Disodium phenyl orthophosphate

Muir, G. D., private comm., 1968

Concentration by evaporation of the nitration product of the phosphate ester caused a violent explosion, possibly involving picric acid derivatives from over-nitration.

Divinyl ether MRH 6.44/22

Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542

Divinyl ether is hypergolic with conc. nitric acid, ignition delay being 1 ms.

See ROCKET PROPELLANTS

Ethanesulfonamide

Suter, C. M., *Organic Chemistry of Sulfur*, 111, London, Wiley, 1944

Reaction with nitric acid at a moderate temperature is explosive, dinitrogen oxide being evolved.

5-Ethyl-2-methylpyridine

1. Frank, R. L., *Chem. Eng. News*, 1952, **30**, 3348
2. Rubinstein, H. *et al., J. Chem. Eng. Data*, 1967, **30**, 3348
3. Elam. E. V. *et al., Chem. Eng. News*, 1973, **51**(34), 42

Following a patented procedure, the two reactants were being heated together at 145°C/14.5 bar to produce 2,5-pyridinedicarboxylic acid. The temperature rose to 160°/43.5 bar, and the autoclave was vented and cooled, but 90 s later a violent explosion occurred, although both rupture disks (rated 105 and 411 bar) had relieved. General precautions are discussed [1]. Up to 20% of 5-(1,1-dinitroethyl)-2-methylpyridine, probably an explosive compound, is produced in this reaction. However, in presence of added water, no instability was seen in a series of reactions at temperatures up to 160°C and pressures up to 102 bar [2]. A further incident in an electrically heated titanium-lined autoclave involved heating the pyridine with excess 70% acid to 140°C during 1 h. When heating was discontinued, the temperature continued to rise in spite of air cooling, and an explosion occurred at 172°C which bulged the autoclave [3]. It is remotely possible that reaction of the titanium liner with the pressurised hot acid may have contributed to the incident.

See Metals (reference 1), below

See also Titanium: Nitric acid

Fat, Sulfuric acid

1. Tyler, L. J., *Chem. Eng. News*, 1973, **51**(31), 32
2. Engan, W. L., *Chem. Eng. News*, 1973, **51**(51), 37

A wet-ashing procedure for analysis of fatty animal tissue was modified by using Teflon-lined bombs rated for use at 340 bar instead of open crucibles. Bombs cooled to well below 0°C were charged with fuming nitric and fuming sulfuric acids (1 ml of each) and adipose tissue (0.5 g), removed from the cooling bath and sealed. After 10 min delay, the bombs exploded, probably owing to development of high internal temperature and pressure (calculated as 4000 K and 1000 bar max.) from complete oxidation of all the organic material [1]. Formation of glyceryl nitrate from the lipid content may have contributed to the violence of the explosion. The presence of 2—5% of water in the mixed acids is recommended to reduce the nitrating potential when in contact with organic fuels [2].

See Organic materials
See Organic materials
See Sulfuric acid

Fluorine MRH 0.50/47
See Fluorine: Nitric acid

Formaldehyde

1. Pirie, C. J. *et al., Chem. Brit.*, 1979, **15**, 11—12
2. Bretherick, L., *CISHC Chem. Safety Summ.*, 1979, **50**(197), 3
3. Vergnano, L. P., *CISHC Chem. Safety Summ.*, 1979, **50**(197), 2
4. Thurger, E. T., *CISHC Chem. Safety Summ.*, 1979, **50**(197), 3
5. Walker, J. F., *Formaldehyde, ACS Monograph 159*, 254—255, New York, Reinhold, 3rd ed. 1964
6. Winsor, L., *Chem. Brit.*, 1979, **15**, 281—282
7. Anon., *Loss. Prev. Bull.*, 1978, (020), 42
8. Haas, P. A., *Chem. Eng. News*, 1987, **65**(16), 2

A closed bottle of decalcifying fluid (a 10% nitric acid—formalin mixture) exploded a few h after the contents had been used and returned to the bottle for storage [1]. The incident was attributed to the interaction of an oxidant with a reducant with evolution of gas, promoted by dissolved impurities arising from its use, leading to pressurisation of the bottle to its bursting point [2,3,4]. This reaction is discussed in detail [5]. 5—10% Solutions of nitric acid or formic acid are preferred decalcifying fluids [6]. After failure of a pump which continuously fed nitric acid into circulating formaldehyde solution (used as a plant cleaning mixture), 30 l of 60% nitric acid was batch-charged into a filter vessel in the fluid circuit. When circulation was restarted to mix in the acid and continue the cleaning operation, a violent redox reaction blew off the lid of the filter vessel [7]. Process development wastes containing urea and hexamethylenetetramine were acidified with nitric acid to dissolve hydrated metal oxides. Under these conditions, hexamine hydrolyses to formaldehyde and ammonium nitrate, and it was calculated that the composition of the acidified waste would be 2M nitric acid, 2M formaldehyde, 1M ammonium nitrate and 0.5M metal nitrate. Such mixtures stored for 2 months in a loosely capped polythene bottle decomposed with vigorous gas evolution which ruptured the container [8].

See other GAS EVOLUTION INCIDENTS, PLANT CLEANING INCIDENTS, REDOX REACTIONS

Formaldehyde, Nicotine
Schindelmeister, J. *Chem. & Ind.*, 2000, (6), 206

An ancient colorimetric test for nicotine is recalled, mixing aqueous formaldehyde, nicotine and concentrated nitric acid. If too much formaldehyde be employed, the test solution turns from red to green and explodes.

Formic acid

Halze, K. *et al., Proc. 3rd. Int. Symp. Loss. Prev. Safety Prom. Proc. Ind.*, 1413—1424, Basle, SSCI, 1980

The use of excess formic acid to destroy excess nitric acid (5M) in nuclear fuel reprocessing waste solutions at 100°C is potentially hazardous because of an induction period, high exothermicity and the evolution of large amounts of gas, mainly carbon dioxide, dinitrogen oxide and nitrogen oxide, with some nitrogen and dinitrogen tetraoxide. The system has been studied thermokinetically, and the effects of various salts (which decrease the reaction rate) and sulfuric acid (which increases the rate) were determined [1].

See other GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS, REDOX REACTIONS

Formic acid, Oxalic acid

Cardillo, P. *et al., Chim. Ind.* (Milan) 1989, **71**(4), 61

A study of, and details of how to control, the stop—start nature of the oxidation of formic acid. Probably relevant to other nitric acid oxidations, especially preparation of glyoxylic acid from glyoxal.

Formic acid, Urea

Mejdell, G. T., *Proc. 3rd. Int. Symp. Loss. Prev. Safety Prom. Proc. Ind.*, 1325—1338, Basle, SSCI, 1980

In the production of formic acid, a slurry of calcium formate in 50% aqueous formic acid containing urea is acidified with strong nitric acid to convert the calcium salt to free acid, and interaction of formic acid (reducant) with nitric acid (oxidant) is inhibited by the urea. When only 10% of the required amount of urea had been added (unwittingly, because of a blocked hopper), addition of the nitric acid caused a thermal runaway (redox) reaction to occur which burst the (vented) vessel. A small-scale repeat indicated that a pressure of 150—200 bar may have been attained. A mathematical model was developed which closely matched experimental data.

See other REDOX REACTIONS, RUNAWAY REACTIONS

2-Formylamino-1-phenyl-1,3-propanediol

1. Biasutti, G. S. *et al., Loss Prev.*, 1974, **8**, 123
2. Biasutti, 1981, 131

Large scale nitration to the *p*-nitro derivative in a stirred and pump-circulated reactor had been effected uneventfully for 15 years when a violent explosion occurred. Subsequent investigation showed that with sufficient priming energy, the reaction mixture could be caused to detonate with an energy release of 3.77 kJ/g [1]. It was supposed that the priming energy originated from a bolt from the agitation gear being sucked into the reactor circulating pump [2].

See other AGITATION INCIDENTS, NITRATION INCIDENTS

Furfural

Giller, S. A. *et al.*, Brit. Pat., 1 466 043, 1977

A safe method of nitrating furfuraldehyde or its *O,O*-diacetate to 5-nitrofurfural diacetate is described which minimises the formation of acetyl nitrate.

Furfurylidene ketones

Panda, S. P. *et al., J. Armam. Stud.*, 1974, **10**(2), 44—45; 1976, **12**, 138—139

In 10 out of 12 cases, furfurylidene derivatives of ketones were hypergolic with red fuming nitric acid. Difurfurylidene hydrazine behaves similarly, and a mechanism involving polymerisation of the compounds is proposed.

Glassware

Anon., *Univ. Saf. Assoc., Saf. Digest*, 1988, (25), 6—8

Nitric acid has long been used to ensure absolute surface cleanliness on laboratory glassware where this is essential for technical reasons. Chromic acid cannot be used for this purpose because a surface film of adsorbed chromium ions remains after cleaning. Following an accident in which some diethyl ether was inadvertently put into the bottle used to store the conc. nitric acid after use and which led to an explosion, a Code of Practice covering the use of acid cleaning procedures for glassware was developed. This proposed that formulated detergents should be used for routine cleaning, and that use of acid processes would only be permitted if it could be practically demonstrated that they were essential for the proposed work. The Code covers the preparation of written procedures dealing with all aspects of the use, storage and disposal of acids, and personal protection requirements.

See Diethyl ether, above;

See CLEANING BATHS FOR GLASSWARE

See other GLASS INCIDENTS

Glycerol

Sanders, R. E., *Chem. Eng. Progress*, 1992, 88(5), 78

Glycerol was inadvertently used as the fluid in a gas bubbler on a nitric acid plant. It nitrated and detonated two days later.

Glycerol, Hydrofluoric acid or Hydrochloric acid

1. Buck, R. H., *J. Electrochem. Soc.*, 1966, **113**, 1352—1353
2. Wright, J. L., private comm., 1984
3. Anon., *Safety Digest Univ. Safety Assoc.*, 1992, **44**, 25

A chemical polishing solution consisting of nitric acid and hydrofluoric acid (1 vol. each) and glycerol (2 vols.) generated enough pressure during storage for 4 h to rupture the closed plastics container. This was caused by gas evolution from oxidation of glycerol by the strongly oxidising mixture [1]. A mixture of nitric acid (80 ml), hydrofluoric acid (80 ml) and glycerol (240 ml) was used immediately for etching metal, again the next day, and then stored in a stoppered flask. After some 2—3 days, the stopper was ejected and 300 ml was sprayed around the fume cupboard containing the flask [2]. The metals dissolved during use further destabilise the mixture, which should not be stored under any circumstances. A freshly made etching mixture with hydrochloric acid, which one would expect to catalyse the oxidant power of nitric acid, burst its bottle in 30 minutes [3].

See Alcohols, above; Hydrofluoric acid, Lactic acid, below

See other GAS EVOLUTION INCIDENTS

Glycerol, Sulfuric acid

Dunn, B. W., *Bur. Expl. Accid. Bull.*, 35, Pennsylvania, Amer. Rail Assoc., 1916

Charging mixed nitrating acid into an insufficiently cleaned glycerol drum led to a violent explosion. Formation and detonation of glyceryl nitrate may have added to the oxidation energy release.

Glyoxal

Urben, P. G., personal experience

The oxidation of aqueous ethanedial to glyoxylic acid is inclined to induction periods and then runaway, cessation and renewed runaway, as the nitric acid is progessively added. Probably this is the same problem as with formic acid, oxalic acid (above).

Hexalithium disilicide

See Hexalithium disilicide: Acids

2,2,4,4,6,6-Hexamethyltrithiane

Baumann, E. *et al., Ber.*, 1889, **22**, 2596

Oxidation of 'tri(thioacetone)' by conc. nitric acid is explosively violent.

See Thioaldehydes, etc., below

2-Hexenal

Lobanov, V. I., *Chem. Abs.*, 1966, **64**, 14013c

Hexenal is determined by photocolorimetry after oxidation with nitric acid. The yellow-orange oxidation product explodes on heating.

Hydrazine and derivatives

1. Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542
2. Jain, S. R., *Combust. Flame*, 1977, **28**, 542
3. Jain, S. R. *et al., J. Spacecr. Rockets*, 1979, **16**, 69—73

Hydrazine is hypergolic with conc. nitric acid [1]. Of a series of hydrazones and azines derived from aldehydes and ketones, only those which decomposed when heated alone were hypergolic with the acid when heated at 12.5°C/min [2]. Solid hydrazones formed from various aldehydes with dimethylhydrazine or phenylhydrazine are hypergolic with the acid [3].

See ROCKET PROPELLANTS

Hydrocarbons MRH Benzene 8.15/18, cyclopentadiene 6.44/18, divinylbenzene 6.23/19, hexane 6.07/18, toluene 6.07/18, *o*-xylene 6.07/17

1. Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542
2. Wilson, P. J. *et al., Chem. Rev.*, 1944, **34**, 8
3. Trent, C. H. *et al., J. Amer. Rocket Soc.*, 1951, **21**, 129—131
4. Ingolgaonkar, M. B. *et al., J. Armam. Stud.*, 1979, **15**(2), 33—42
5. Sykes, W. G. *et al., Chem. Eng. Progr.*, 1963, **59**(1), 70—71
6. Mason, C. M. *et al., J. Chem. Eng. Data*, 1965, **10**, 173
7. Urbanski, 1961, Vol. 1, 140
8. Derbyshire, D. H., *Proc. 1st Symp. Chem. Process Haz. Ref. Plant Des.*, 37—41, Symp. Ser. No. 7, London, IChE, 1960
9. Powell, G. *et al., Org. Synth.*, 1943, Coll. Vol. 2, 450
10. Wilms, H. *et al., Angew. Chem.*, 1962, **74**, 465
11. Chaigneau, M. *Compt. rend.*, 1951, **223**, 657—659
12. Anon., *Chemisches Ind.*, 1914, **37**, 337—342

13. Biasutti, 1981, 48
14. Bryant, T. J. *et al., Rept. AD-B-000447*, Richmond (Va.), USNTIS, 1974
15. Panda, S. P. *et al., Chem. Abs.*, 1981, **94**, 194475
16. Dutta, P. K. *et al., J. Armam. Stud.*, 1976, **12**, 108—117
17. Mellor, 1964, Vol. 8, Suppl. 2, 341

Dienes and acetylene derivatives are hypergolic in contact with conc. nitric acid, ignition delay being 1 ms [1]. Cyclopentadiene reacts explosively with fuming nitric acid [2], igniting under nitrogen [3], and dicyclopentadiene is highly hypergolic with red or white fuming nitric acid, also in presence of sulfuric acid [4]. Burning fuel oil and other petroleum products detonate immediately on contact with conc. nitric acid [5]. Very high sensitivity is shown by mixtures with benzene close to the stoicheiometric proportions of around 84% acid [6]. Lack of proper control in nitration of toluene with mixed acids may lead to runaway or explosive reaction. A contributory factor is the oxidative formation, and subsequent nitration and decomposition, of nitrocresols [7]. Oxidation of *p*-xylene with nitric acid under pressure in manufacture of terephthalic acid carries explosion hazards in the autoclaves and condensing systems [8]. During nitration of mesitylene in acetic acid—acetic anhydride solution, fuming nitric acid must be added slowly to the cooled mixture to prevent the temperature exceeding 20°C, when an explosive reaction may occur [9]. During oxidation of mesitylene with nitric acid in an autoclave at 115°C to give 3,5-dimethylbenzoic acid, a violent explosion occurred. This was attributed to local overheating, formation of 1,3,5-tris(nitromethyl)benzene and violent decomposition of the latter. Smaller scale preparations with better temperature control were uneventful [10].

The explosive hazards involved in the preparation of mellitic acid by fuming nitric acid oxidation of hexamethylbenzene make the procedure only suitable for small scale operation [11]. Large-scale addition of too-cold nitrating acid to benzene without agitation later caused an uncontrollably violent reaction to occur when stirring was started. The vapour—air mixture produced was ignited by interaction of benzene and nitric acid at 100—170°C and caused an extremely violent explosion [12]. Failure to start the agitator or to apply water cooling in nitration of benzene led to a pressure burst of the nitrating vessel [13]. In the impact-initiated combustion of hydrocarbons in acid at high pressure, the effects of impact, hydrocarbon structure and stoicheiometry upon ignition were studied [14]. The pure terpene 3-carene is more hypergolic with red fuming nitric acid than the mixture with other terpenes in turpentine [15]. The use of turpentine and cashew nutshell oil as bases for hypergolic rocket fuels with red fuming nitric acid has been evaluated [16]. The nitric acid—gasoline propellant system is non-hypergolic, but can be made so by addition of 15—25% of unsaturated hydrocarbons to the gasoline [17].

See other AGITATION INCIDENTS, NITRATION INCIDENTS

Hydrocarbons, 1,1-Dimethylhydrazine

Ingolgaonkar, M. B. *et al., J. Armam. Stud.*, 1979, **15**(2), 33—42

Presence of the hydrazine confers hypergolicity upon mixtures of several non-hypergolic hydrocarbons with red fuming nitric acid.

Hydrofluoric acid, Lactic acid

Bubar, S. F. *et al., J. Chem. Educ.*, 1966, **43**, A956

Mixtures of the 3 acids, used as metal polishing solutions, are unstable and should not be stored. Lactic acid and nitric acid react autocatalytically after a quiescent period, attaining a temperature of about 90°C with vigorous gas evolution after about 12 h. Prepare freshly, discard after use and handle carefully.

See Glycerol, etc., above

See other INDUCTION PERIOD INCIDENTS

Hydrofluoric acid, Propylene glycol, Silver nitrate

Leleu, *Cahiers*, 1979, (94), 125

A chemical polishing mixture was put into a closed glass bottle which burst 30 min later, and formation of silver fulminate was suggested. However, in absence of the silver salt such mixtures evolve gas and should not be stored in any event, especially after use for metal polishing, when the dissolved metal(s) tend to further destabilise the mixture.

See Glycerol, etc., above

Hydrogen iodide, or Hydrogen selenide, or Hydrogen sulfide

See Non-metal hydrides, below

Hydrogen peroxide, Ketones

See Hydrogen peroxide, Ketones, etc.

Hydrogen peroxide, Mercury(II) oxide

See Hydrogen peroxide: Mercury(II) oxide, etc.

Hydrogen peroxide, Soils

Krishnamurty, K. V. *et al., At. Abs. Newslett.*, 1976, **15**, 68—70

When preparing soil and sediment samples for atomic absorption spectral analysis for trace metals, pre-oxidation with nitric acid before addition of hydrogen peroxide eliminates the danger of explosion.

Ion exchange resins

1. Barghusen, J. *et al., Reactor Fuel Process.*, 1964, **7**, 297
2. McBride, J. A. *et al., 3rd Geneva Conf. Peaceful Uses At. En. A/CONF. 28 28/P/ 278*, 1965
3. Kalkworf, D. R., *Rept. BNWL-2931*, Richland (Wa.), Battelle, 1977
4. Colman, C., *Chem. Eng*. (New York), 1980, **87**, 271—274

Several cases of interaction between anion exchange resins and nitric acid causing rapid release of energy or explosion have occurred [1]. The cause has been attributed to oxidative degradation of the organic resin matrix and/or nitration of the latter. Suggested precautions include control of temperature, acid concentration and contact time. Presence of heavy ions (Pu) or oxidising agents (dichromates) tends to accelerate the decomposition [2]. The present state of knowledge was reviewed and relevant process parameters identified [3]. Several case histories are given, and safety aspects of regeneration of large-volume beds of strong-base anion exchange resins or cationic exchangers with nitric acid are discussed, but weak-base resins should not be treated with nitric acid. Storage of nitric acid-containing resins may lead to ignition [4].

See other SELF-HEATING AND IGNITION INCIDENTS

Iron(II) oxide

Mellor, 1941, Vol. 13, 716

The finely divided (pyrophoric) oxide incandesces with nitric acid.

Lead-containing rubber

Johnson, T. C. *et al., Rep. RFP-1354*, 1—8, Washington (DC), USAEC, 1969

Radiation resistant lead-containing dry-box gloves may ignite in nitric acid environments.

Magnesium phosphide

Mellor, 1940, Vol. 8, 842

Oxidation of the phosphide proceeds with incandescence.

Magnesium silicide

Mayes, R. B. *et al., School Sci. Rev.*, 1975, **56**(197), 819—820

When the residue from combustion of magnesium in air was removed from the porcelain crucible, a grey stain remained. Addition of cold conc. nitric acid to remove the stain led to a violent reaction. This was found to be caused by the presence of magnesium silicide in the stain.

Magnesium, 2-Nitroaniline

Gune, S. G. *et al., J. Armam. Stud.*, 1983, **18—19**, 39—41

Though neither of the components is individually hypergolic with red fuming nitric acid, mixtures with magnesium containing 20% and 30% of 2-nitroaniline ignite with 67 and 23 ms delay, respectively.

Manufacture hazard

Lawrence, G. M., *Plant/Oper. Progr.*, 1989, **8**(1), 33

An explosion in the vent of an ammonia combustion plant was attributed to deposition of ammonium nitrite/nitrate crystals. It is considered that the very unstable nitrite acts as a sensitiser to the nitrate, and that explosion is triggered by contact with acid.

See Ammonium nitrate, Ammonium nitrite

Metal acetylides

Mellor, 1946, Vol. 5, 8482

Caesium acetylide and rubidium acetylide explode in contact with nitric acid, and the sodium and potassium analogues probably react violently.

Metal cyanides

491M, 1975, 268

Explosive reactions.

Metal hexacyanoferrates

Sidgwick, 1950, 1344

The action of 30% nitric acid on hexacyanoferrates(II) or (III) to produce pentacyanonitrosylferrate(II) (‘nitroprusside’) is violent.

Metal salicylates

Belcher, R., private comm., 1968

Metal salicylates are occasionally incorporated into mixtures of ‘unknowns’ for qualitative inorganic analysis. During the conventional group separation, organic radicals are removed by evaporation with nitric acid. When salicylates are present, this can lead to formation of trinitrophenol through nitration and decarboxylation. This may react with any heavy metal ions present to form unstable or explosive picrates, if the evaporation is taken to dryness. The MAQA alternative scheme of analysis obviates this danger.

See Lead(II) picrate

Metal thiocyanate MRH Potassium thiocyanate 4.31/42

MCA Case History No. 853

When the (unspecified) thiocyanate solution was pumped through an 80 mm pipeline containing nitric acid, a violent explosion occurred. This was confirmed experimentaly and attributed to the redox reaction between the reducing solution and the oxidant acid.

See other REDOX REACTIONS

Metals MRH Calcium 9.33/61, lithium 15.27/40, magnesium 11.96/48, manganese 4.88/59, nickel 2.64/70, sodium 5.48/64, zinc 3.60/72

1. Mellor, 1940, Vol. 2, 470; 1940, Vol. 4, 270, 483; 1941, Vol. 7, 260; 1940, Vol. 9, 627; 1942, Vol. 12, 32, 188
2. Pascal, 1956, Vol. 10, 504
3. Condike, G. F., *Chemistry*, 1974, **47**(4), 27—28
4. McGarman, A. R., *Chemistry*, 1974, **47**(11), 27—28

Bismuth powder glows red-hot in contact with fuming nitric acid, while the molten metal (271°C) explodes in contact with conc. acid. Powdered germanium reacts violently with the latter, and lithium ignites. Manganese powder incandesces and explodes feebly with nitric acid, and sodium ignites with nitric acid of density above 1.056. Titanium alloys form an explosive deposit with fuming nitric acid. Although uranium powder reacts vigorously with red fuming nitric acid, under some conditions explosive deposits may be formed. Addition of conc. acid to molten zinc (419°C) causes it to incandesce, and magnesium burns brilliantly in nitric acid vapour [1]. Antimony may be attacked violently by fuming nitric acid [2]. The experimental quantities of tin and nitric acid specified for a laboratory demonstration [3] are likely to lead to formation of the explosive nitrate oxide [4].

See Copper, above

See Tetrahydroxotritin(2+) nitrate, Silver nitrate: Titanium

Methanol, Sulfuric acid

Anon., *Chem. & Ind.*, 1986, 725

A nitration reactor was charged with methanol which was wrongly labeled as xylene. Addition of nitrating acid mixture led to a runaway exothermic reaction which eventually ruptured the reactor as well as the bursting disk, allowing 2700 l of mixed acid to spray out.

See Alcohols, above

See other NITRATION INCIDENTS

2-Methoxyethylbenzene, Sulfuric acid

Urben, P. G., personal experience

This substrate, dissolved in 3 molar equivalents of sulfuric acid, was batch nitrated by slow addition of 1.05 moles of concentrated nitric acid at 5—20°C followed by a stir-out and quenching into water. No problems were seen in the laboratory but on pilot plant (½ kilomole) there was twice a sharp exotherm 2½ hours after completion of addition, blowing the bursting disk with gas evolution, leaving 4-nitrobenzoic acid as the (minor) isolable product. With good thermal insulation and poor agitation it was possible to reproduce this in the lab. No evidence of dinitration could be found and mononitration appeared almost instantaneous. Reduction of the nitric acid to 0.99 equivalents prevented recurrence, even on a much larger scale with day long delays, while not changing the near quantitative yield.

The end point corresponded to generation of sulfuric acid monohydrate; the experimenter subsequently adopted the rules of thumb that oxidative side reactions do not occur while the availability of water is less than this, and that dinitration sideproducts are a consequence of charging substrate, traditionally but irrationally, to nitration mixture.

See other NITRATION INCIDENTS

2-Methylbenzimidazole, Sulfuric acid

Zmojdzin, A. *et al.*, Ger. Offen. 2 310 414, 1974

A safe method of preparing 5-nitro-2-methylbenzimidazole involves preliminary addition of the heterocycle to nitric acid (*d* 1.40) with subsequent addition of sulfuric acid, keeping the temperature below 110°C.

See other NITRATION INCIDENTS

4-Methylcyclohexanone

Dye, W. T., *Chem. Eng. News*, 1959, **37**, 48

Oxidation of 4-methylcyclohexanone by addition of nitric acid at about 75°C caused a detonation to occur. These conditions had been used previously to oxidise the corresponding alcohol, but although the ketone is apparently an intermediate in oxidation of the alcohol, the former requires a much higher temperature to start and maintain the reaction. An OTS report, PB73591, mentions a similar violent reaction with cyclohexanone.

See Acetone, etc., above

Methylthiophene

Rüst, 1948, 318

During the nitration of methylthiophene, direct liquid contact caused ignition to occur, so air saturated with the organic vapour was passed into the cooled conc. acid. After a while, the whole apparatus exploded violently, probably owing to ignition of the air—fuel mixture being passed in.

See Thiophene, below

See other NITRATION INCIDENTS

Molybdenum nitride

See Molybdenum nitride: Nitric acid

Naphthalene-1-sulfonic acid, Sulfuric acid

Anon. *Loss Prev. Bull.*, 1994, (116), 21

Production of dye intermediates by nitration of the sulfonic acid was conducted under automatic control, nitric acid being added automatically so long as the temperature was below 30°C. There was no other control on nitric acid addition. The agitation and probably also the thermocouple reading being inadequate, excess nitric acid appears to have charged, layered, then reacted, blowing apart the vessel.

See other AGITATION INCIDENTS

Nitroaromatics MRH Nitrobenzene 6.32/29, nitroxylene 6.23/25, dinitrobenzene 5.02/99+, 2,4-dinitrotoluene 4.56/99+

1. Urbanski, 1967, Vol. 3, 290
2. Raikova, V. M., *Chem. Abs.*, 1983, **98**, 5958

A series of mixtures of nitric acid with one or more of mono-and di-nitrobenzenes, di- and tri-nitrotoluenes have been shown to possess high-explosive properties [1]. Critical detonation diameters for mixtures of nitric acid with dinitrotoluene and TNT have been determined [2].

Nitrobenzene, Sulfuric acid

Fritz, E. J., *Loss Prev.*, 1969, **3**, 41—44

Failure of the agitator during addition of mixed nitrating acid allowed unreacted reagents to build up in the reaction system which, owing to absence of the usual reaction exotherm, became under-cooled. Application of heat and agitation caused a runaway reaction, terminating in explosion, to occur. Laboratory-scale repetition of this sequence showed an exotherm to 200°C in 0.1 s, a rate of almost 2000°/s. Operating improvements are detailed.

See other AGITATION INCIDENTS, NITRATION INCIDENTS, RUNAWAY REACTIONS

Nitrobenzene, Water

1. Anon., J. R. *Inst. Chem.*, 1960, **84**, 451
2. Van Dolah, R. W., *Loss. Prev.*, 1969, **3**, 32

A plant explosion involved a mixture of nitrobenzene, nitric acid and a substantial quantity of water. Detonation occurred with a speed and power comparable to TNT. This was unexpected in view of the presence of water in the mixture [1]. The later reference deals with a detailed practical and theoretical study of this system and determination of the detonability limits and shock-sensitivity. The limits of detonability coincided with the limits of miscibility over a wide portion of the ternary composition diagram. In absence of water, very high sensitivity (similar to that of glyceryl nitrate) occurred between 50 and 80% nitric acid, the stoicheiometric proportion being 73% [2].

See Nitroaromatics, above

Nitromethane MRH 6.19/62

Olah, G. A. *et al., Org. Synth.*, 1957, **47**, 60

Mixtures are extremely explosive.

1-Nitronaphthalene, Sulfuric acid

Biasutti, 1981, 83

Towards the end of nitration of mononitronaphthalene to trinitronaphthalene, a drain valve became blocked with tarry solid. Raising the temperature to 60°C to melt the obstruction led to separation of more solid, failure of the agitator, then a runaway reaction and detonation.

See other AGITATION INCIDENTS, NITRATION INCIDENTS, RUNAWAY REACTIONS

Non-metal hydrides

1. Mellor, 1946, Vol. 5, 36; 1940, Vol. 6, 814; 1939, Vol. 9, 56, 397
2. Hofmann, A. W., *Ber.*, 1870, **3**, 658—660
3. Pascal, 1956, Vol. 10, 505

Arsine, phosphine and tetraborane(10) are all oxidised explosively by fuming nitric acid, while stibine behaves similarly with the conc. acid [1]. Hydrogen iodide, hydrogen selenide, hydrogen sulfide and phosphine all ignite when the fuming acid is dripped into the gas [2]. Hydrogen telluride ignites with cold conc. acid, sometimes exploding [3].

See Ammonia, above; and Phosphine derivatives, below

Non-metals

1. Mellor, 1946, Vol. 5, 16; 1940, Vol. 8, 787, 845
2. Bailar, 1973, Vol. 1, 1337
3. Pascal, 1956, Vol. 10, 504
4. *MCA Case History No. 1969*

Boron (finely divided forms) reacts violently with conc. acid and may attain incandescence. The vapour of phosphorus, heated in nitric acid in presence of air, may ignite. Boron phosphide ignites with the conc. acid [1]. Silicon crystallised from its eutectic with aluminium reacts violently with conc. acid [2], arsenic may react violently with the fuming acid, and finely divided carbon similarly with conc. acid [3]. Use of conc. acid to clean a stainless steel hose contaminated with phosphorus led to an explosion [4].

Oleoyl chloride

Nolan, 1983, Case history 62

3-Nitro-4-cresol was to be manufactured by adding 4-toluidine to nitric acid. One carboy of nitric acid was charged into the reactor, but the next one charged actually contained oleoyl chloride in error. The violent reaction ensuing ruptured the reactor and there was a fire.

See other NITRATION INCIDENTS

Organic diacids

See Cyclohexanol, Cyclohexanone, above

Organic materials

1. Bowen, H. J. M., private comm., 1968
2. Turnbull, A. J., *Chem. Brit.*, 1979, **15**, 377
3. Williams, E. V., *J. Food Technol.*, 1978, **13**, 167
4. Everson, R. J., *Chem. Eng. News*, 1980, **58**(11), 5
5. Coleman, C. B., *Chem. Eng. News*, 1980, **58**(11), 5
6. Katz, S. A., *Chem. Eng. News*, 1980, **58**(17), 51

7. Borgaard, O. K. *et al., J. Assoc. Offic. Anal. Chem.*, 1982, **65**, 762—763
8. Anon., *Inst. Univ. Safety Officers Bull.*, 1987, (8), 9
9. Ward, N. I., *Internat. Analyst*, 1987, **1**(2), 7

When 16 M (70%) nitric acid was poured down a sink without diluting water, interaction with (unspecified) organic material in the trap caused a delayed explosion [1]. Digestion of biological materials with nitric acid in Teflon-lined bombs has led to several violent explosions. A suggested improvement was to leave the sample in contact with nitric acid overnight before sealing and heating the bomb [2]. An alternative procedure of digesting samples with nitric acid at 20°C for 24 h in polystyrene tubes with hand-tightened polythene screw caps [3] also led to explosions when generous samples of dry-powdered food products were digested [2]. Digestion of 0.8 g of dry dog-food with 5 cc of nitric acid at 130°C in Teflon lined stainless bombs led to explosions [4], or of 0.2 g of sewage sludge with 2.5 cc of acid [5]. The amount of organic material is normally restricted to 0.1 g in the bomb manufacturer's instructions [6]. Note that 0.1 g of carbon on oxidation with nitric acid gives a minimum volume of 540 cc of gas measured at 1 bar/120°C, so a static pressure of many bar would be attained in a 10—20 cc bomb. The hazards of digesting organic samples with nitric acid in closed systems for elemental analysis have been stressed. Digestion in an open flask may be a safer alternative in many cases [7]. In preparation for the analysis of powdered milk for trace metals, 1 g portions were heated at 80°C with 5 ml of conc. nitric acid in 25 ml Teflon lined stainless digestion vessels made to a design maximum of 500 bar, with maximum working pressure limited to 125 bar. With all 3 samples explosions occurred, rupturing the digestion vessels and causing local damage. In one account of the incident, the explosions were attributed to formation of glyceryl trinitrate [8], but this is extremely unlikely, as its formation normally requires presence of conc. sulfuric acid as dehydrating agent. In a second account the correct explanation of a runaway exothermic oxidation reaction of an excessive sample by undiluted nitric acid accompanied by gas formation was deduced. The strong recommendation to limit sample size to 0.1 g maximum [9] coincides with that made 7 years previously [6].

See other GAS EVOLUTION INCIDENTS

Organic materials, Perchloric acid

See Perchloric acid: Nitric acid, etc.

Organic materials, Potassium chlorate

See Potassium chlorate: Nitric acid, etc.

Organic materials, Sulfuric acid

Anon., *ABCM Quart. Safety Summ.*, 1934, **5**, 17

Use of the mixed conc. acids to dissolve an organic residue caused a violent explosion. Nitric acid is a very powerful and rapid oxidant and may form unstable fulminic acid or polynitro compounds under these conditions.

Other reactants

Yoshida, 1980, 188—189

MRH values calculated for 28 combinations, largely with oxidisable materials, are given.

Phenylacetylene, 1,1-Dimethylhydrazine

Spengler, G. *et al., Sci. Tech. Aerospace Rept.*, **2**(17), 2392, Washington, NASA, 1964

Phenylacetylene does not itself ignite on contact with nitric acid, but addition of 1,1-dimethylhydrazine renders it hypergolic.

See Hydrocarbons, above

Phosphine derivatives MRH Ethylphosphine 6.15/23

1. von Schwartz, 1918, 325
2. Mellor, 1947, Vol. 8, 827, 1041
3. Graham, T., *Trans. Roy. Soc. Edinburgh*, 1835, **13**, 88

Phosphine ignites in conc. nitric acid and addition of warm fuming nitric acid to phosphine causes explosion [1]. Phosphonium iodide ignites with nitric acid, and ethylphosphine explodes with fuming acid [2]. Tris(iodomercuri)phosphine is violently decomposed by nitric acid or aqua regia [3].

Phosphorus compounds

Mellor, 1947, Vol. 8, 1061; 1971, Vol. 8, Suppl. 3, 348, 335, 373

Tetraphosphorus tetraoxide trisulfide or neodymium phosphide are violently oxidised, nickel tetraphosphide ignites with the fuming acid, and tetraphosphorus diiodo triselenide reacts explosively with nitric acid.

See 2-Alkoxy-1,3-dithia-2-phospholane, above

Phosphorus halides

Mellor, 1947, Vol. 8, 827, 1004, 1038

Tetraphosphorus iodide ignites in contact with cold conc. nitric acid, and phosphorus trichloride explodes with nitric (or nitrous) acid.

Phthalic anhydride, Sulfuric acid

1. Tyman, J. H. P. *et al., Chem. & Ind.*, 1972, 664
2. Bentley, R. K., *Chem. & Ind.*, 1972, 767
3. Bretherick, L., *Chem. & Ind.*, 1972, 790

Attempts to follow a published method for nitrating phthalic anhydride in sulfuric acid at 80—100°C with fuming nitric acid caused an eruptive decomposition to occur after 2 h delay [1]. The hazard can be eliminated by use of a smaller excess of nitrating acid at 55—65°C [2]. Acyl nitrates were suggested as a possible cause of the delayed eruption [3].

See Sulfuric acid, Terephthalic acid, below

Polyalkenes

1. Marsh, J. R., *Chem. & Ind.*, 1968, 1718
2. Dabeka, R. W. *et al., Anal. Chem.*, 1976, **48**, 2048
3. Kaufman, J. A., private comm., 1987
4. Weker, R. A. *et al., Chem. Eng. News*, 1995, **73**(25), 4

Fuming nitric acid had seeped past the protective polytetrafluoroethylene liner inside the polyethylene or polypropylene screw cap and attacked the latter, causing pressure build-up in the glass bottle [1]. Polypropylene bottles are unsuitable for long term storage of nitric acid, because slow embrittlement and cracking occur [2]. A plastic bottle (polythene?) used to store conc. nitric acid collapsed while being carried [3]. Digestion of airborne particulate metals caught on a PTFE filter by nitric acid in a microwave oven led to explosion. The filter membrane was mounted in a poly(methylpentene) support, which was the cause of the violent reaction. Use of either an all PTFE filter, or cutting away the support ring, is advisable [4].

Poly(dibromosilylene)
See Poly(dibromosilylene): Oxidants

Poly(ethylene oxide) derivatives
1. Corby, M. P., *Chem. Brit.*, 1975, **11**, 334; private comm., 1975
2. Corby, M. P., *Chem. Brit.*, 1975, **11**, 456

A mixture of nitric and phosphoric acids (50, 17%, respectively) with a primary alcohol ethoxylate surfactant (0.1%) and water exploded after storage for 7 months in a glass bottle [1]. Progressive hydrolysis under these conditions would be expected to lead to production of the readily oxidised ethylene glycol, and gaseous decomposition products leading to pressure build-up. A general warning against mixing surfactants and oxidising acids is given [2]. The formation of ethylene glycol dinitrate is perhaps unlikely in view of the 33% water content in the mixture.

Polymer (unspecified)
Anon., *Safety Digest Univ. Safety Assoc.*, 1989, **34,** 14
Throat cut, almost fatally, by shards of a test tube from which a polymeric residue was being cleared. Explosion apparently almost immediate; were there also miscible solvent residues?

Poly(silylene)
See Poly(silylene): Oxidants

Polythene, Steel
U.S. Dept of Environment, DOE/ORO/2061, 1997
A polythene-lined steel drum, packed within a steel drum and then another lined steel drum, was left filled with nitric acid for almost 40 years. It eventually exploded, some three months after sampling (which would have vented it). This was attributed to embrittlement of the liner, allowing acid to seep through, accelerated by damage during sampling, and attack the steel of both the primary and secondary drum. Although the accident is explained entirely in terms of nitric acid and steel, there was also radioactive waste (unspecified) in the nitric acid - and it seems possible that even the innermost drum might have had oxidisable labelling or coating on its exterior surface.
See also NUCLEAR WASTES

Polyurethane foam
Anon., *Loss Prev. Bull.*, 1980, (035), 10—11
Mechanical cleaning of a multitubular stainless steel condenser (blocked by a rigid polyurethane foam) by rodding the tubes was laborious, so chemical cleaning with conc. nitric acid was attempted. When the initial vigorous reaction (‘fireworks’) subsided, owing to crust formation, the rod was again inserted, but a sudden explosion occurred which ruptured the condenser.
See other PLANT CLEANING INCIDENTS

Preparative hazard

Crawley, F. K., *Loss Prev. Bull.*, 1992, (104), 4

Corrosion permitted leak of nitric acid into the ammonia feed passing through the cooling tubes of a nitric acid plant. An ammonium nitrate deposit built up and exploded when the tubes were cut out with a welding torch for replacement.

Propiophenone, Sulfuric acid

1. Baker, J. W., *J. Chem. Soc.*, 1932, 1155
2. Dowell, R. I., *Chem. Brit.*, 1981, **17**, 56—57
3. Keneford, J. R., *et al., J. Chem. Soc.*, 1948, 356

During the nitration of propiophenone following a published procedure [1] by adding the ketone to the mixed acids at —5 to 0°C, an uncontrollable exotherm developed and finally accelerated to explosion [2]. The nitration was subsequently effected by an alternative procedure operated at —10 to —5°C [3].

See other NITRATION INCIDENTS

Pumps

Anon. *Loss Prev. Bull.*, 1994, 116, 21

Two incidents of pump explosions in chemical plants are reported, both occasioned by nitric acid reaching parts of a pump it should not and there corroding metal or contacting electrics. Proper pump selection, installation and maintenance would have avoided these incidents.

Pyrocatechol

Andrussow, L., *Chim. Ind.* (Paris), 1961, **86**, 542

The phenol is hypergolic with conc. nitric acid, with a 1 ms ignition delay.

Reducants

A variety of reducants ignite or explode with nitric acid.

See Hydrazine and derivatives, above

See Hydrogen sulfide: Oxidants

See Non-metal hydrides, above

See Potassium phosphinate: Air, or Nitric acid

See Sulfur dioxide, below

Resorcinol

Biasutti, 1981, 104

During the preparation of dinitroresorcinol, too low a concentration of nitric acid (82%) led to formation of tarry material, some of which remained in the nitrator discharge line. In the following batch, the tar decomposed in contact with higher strength acid, leading to an explosion.

See other NITRATION INCIDENTS, PLANT CLEANING INCIDENTS

Rubber

1. Read, T. R., *School Sci. Rev.*, 1976, **57**(200), 592
2. Mishra, B. *et al., J. Hazard. Mater.*, 1997, 56, 107

In a demonstration of the corrosive effect of fuming nitric acid on rubber tubing, soon after the initial vigorous reaction had subsided, a small explosion followed by ignition occurred. (The sulfur compounds used to compound the rubber were probably

involved) [1]. Leaded neoprene rubber gloves, (the lead present as red lead, Pb_3O_4) used in the nuclear industry, may form explosive compounds in contact with nitric acid. It is hypothesised this could be lead fulminate formation. Since mixtures of lead nitrate with organics, or with sulfur from vulcanisers, would be explosive, this seems unduly complicated [2].
See other CORROSION INCIDENTS

Salicylic acid
See Lead(II) picrate

Silicone oil
Phillips, C. V. *et al., Lab. Pract.*, 1981, **30**, 598
A mineral was being leached by heating with 7 M nitric acid in a PTFE-lined bomb heated by immersion in a silicone oil bath, and at 195°C a violent explosion occurred. This was attributed to prior leakage of oil into the pressure vessel, which had been immersed in the oil at 120°C, then allowed to cool, before being heated to the higher temperature. Appropriate precautions are recommended.

Silver buten-3-ynide
See Silver buten-3-ynide: Alone, or Ammonia, etc.

Steel gas cylinder
Anon., *CISHC Chem. Safety Summ.*, 1974—5, **45—46**, 3—4
Conc. nitric acid leaking from a faulty road tanker became partially diluted with water and was prevented from running away along the roadside gully by a full oxygen cylinder in the horizontal position. After several h, the cylinder was sufficiently weakened by corrosion to split open under the internal gas pressure.
See other CORROSION INCIDENTS

Sucrose
Poncini, L., *School Sci. Rev.*, 1981, **62**(200), 515—516
Use of aqueous solutions of sucrose rather than the solid in class demonstrations of preparation of oxalic acid is described as safer.

Sulfur dioxide
Coleman, G. H. *et al., Inorg. Synth.*, 1939, **1**, 55
Presence of dinitrogen tetraoxide appears to be essential to catalyse smooth formation of nitrosylsulfuric acid from sulfur dioxide and nitric acid. In its absence, reaction may be delayed and then proceed explosively.
See other CATALYTIC IMPURITY INCIDENTS

Sulfur halides
Mellor, 1947, Vol. 10, 646, 651—652
Interaction with sulfur dichloride, sulfur dibromide or disulfur dibromide is violent, the hydrogen halide being liberated.
See other GAS EVOLUTION INCIDENTS

Sulfuric acid
1. Anon., *BCISC Quart. Safety Summ.*, 1964, **35**, 3
2. *FPA H50*, 1976; *HCS 1980*, 666

The gland of a centrifugal pump being used to pump nitrating acid (nitric:sulfuric, 1:3) exploded after 10 min use. This was attributed to nitration of the gland packing, followed by frictional detonation. Inert shaft sealing material is advocated [1]. General handling precautions for nitrating acid are detailed [2].
See 2,2-Oxybis(ethyl nitrate)

Sulfuric acid, Terephthalic acid
Withers, C. V., *Chem. & Ind.*, 1972, 821; private comm., 1972
During nitration of the acid with fuming nitric acid in oleum, a delayed exotherm increased the temperature after 2 h from 100° to 160°C, causing eruption of the contents. At 120° the delay was 1 h and at 130°C, 30 min.
See Phthalic anhydride, etc., above
See other INDUCTION PERIOD INCIDENTS

Sulfuric acid, thioanisole
MARS Database, Short Report, Accident No. 033
A serious explosion, breaking windows up to 700 metres distant (implying considerable TNT equivalence) was consequent upon charging sulfuric and nitric acids in the wrong order (unspecified) when nitrating the aromatic. [The editor would incline to charging first sulfuric, then thioanisole, and finally, slowly, the nitric. Mixing the highly oxidant nitric with the, seriously reducing, sulfide in the absence of strong acid catalyst and dehydrating agent to promote nitration would surely lead to autocatalyic oxidation after a short induction period]. There was a runaway and explosion, which latter this report attributes to methyl nitrate byproduct entering the attached condenser and there exploding. Damage being described as total destruction of the production unit, thus far from restricted to the condenser, such explanation seems unduly specific.
See other NITRATION INCIDENTS

Sulfuric acid, Toluene
Chen, C-Y. *et al., Trans. IChemE.*, 1998, **76**(B), 211
Displaying a grasp of chemistry remarkable even among chemical engineers, the authors ascribe the hazardous side reaction consequent upon mono-nitration of toluene in mixed acid, to a decomposition of nitric acid (science has hitherto regarded nitric acid as thermodynamically more stable than conceivable decomposition products). This is favoured by poor mixing in what they describe as a three phase mixture (*mixo*-nitrotoluenes being apparently immiscible with toluene). What the calorimetric study described seems to have observed is the transition from nitration to oxidation of the substrate.
See other NITRATION INCIDENTS

Tetrabromomethane, Hydrochloric acid.
Chilman, K., Mineral Resources (New South Wales) Safety Alert: SA99/09, 1999
A bottle containing these three blew its lid on standing, spraying the contents around the lab. Nitric acid is surely capable of oxidising the halocarbon, but slow pressurisation with chlorine is also possible.

Thioaldehydes, or Thioketones
Campaigne, E., *Chem. Rev.*, 1946, **39**, 57

Nitric acid generally reacts too violently with thials or thiones for the reactions to be of preparative interest.

Thiols
See Alkanethiols, above

Thiophene
1. Meyer, V., *Ber.*, 1883, **16**, 1472
2. Babasinian, V. S., *Org. Synth.*, 1944, Coll. Vol. 2, 467

Interaction of thiophene with fuming nitric acid is very violent if uncontrolled, extensive oxidation occurring [1]. Use of a diluent and close control of temperature is necessary for preparation of nitrothiophene [2].
See Methylthiophene, above

1,3,5-Triacetylhexahydro-1,3,5-triazine, Trifluoroacetic anhydride
1. Albright and Hanson, 1976, 327
2. Bedford, C. D., *Chem. Eng. News*, 1980, **58**(35), 33, 43
3. Gilbert, E. E., *Chem. Eng. News*, 1980, **58**(40), 5
4. Bretherick, L., *Chem. Eng. News*, 1981, **59**(14), 59

During the attempted nitrolysis of the triacetyl compound to the 1-acetyl-3,5-dinitro compound with 99% nitric acid in trifluoroacetic anhydride at 30°C, following a general procedure [1], a violent explosion occurred on the 1 g scale [2]. This was ascribed to the formation of acetyl nitrate, expected to be formed under the reaction conditions [3,4]. Caution with nitrolysis of any acetyl compound is urged [3].
See Acetic anhydride, above; Triazine, etc., below

Triazine, Trifluoroacetic anhydride
491M, 1975, 272
N-Nitration of triazine with 99% nitric acid in trifluoroacetic anhydride at 36°C proceeded explosively.

Tributyl phosphate
Ruyat, Y. et al., Chem. Abs., 2003, **139**, 383563d
Although best known as a tool and hazard in actinide separation for nuclear reprocessing, the mix is evaluated as a Sprengel explosive.
See NUCLEAR WASTES

Triethylgallium etherate
See Triethylgallium

2,4,6-Trimethyltrioxane
Muir, G. D., private comm., 1968
Oxidation of the trioxane (‘paraldehyde’) to glyoxal by action of nitric acid is subject to an induction period, and the reaction may become violent if addition of the trioxane is too fast. Presence of nitrous acid eliminates the induction period.
See other INDUCTION PERIOD INCIDENTS

Turpentine
Hermoni, A., *Appl. Chem.*, 1958, **8**, 670—672

Turpentine and fuming nitric acid do not ignite on contact in absence of added catalysts (fuming sulfuric acid, iron(III) chloride, ammonium metavanadate or copper(II) chloride).
See Hydrocarbons, above

Uranium disulfide
Sidgwick, 1950, 1081
Interaction is violent.

Wastes
Now that solvents are collected in laboratories and stored in bottles for appropriate later disposal, rather than tipped to darin, nitric acid is sometimes treated as just another solvent. The result is usually an explosion.

Wood

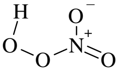
1. Personal experience, 1974
2. Anon., *Chem. Eng. News*, 1975, **53**(11), 14
3. *MCA Case History No. 1797*
4. Anon., *Chem. & Ind.*, 1994, (6), 212

A cracked winchester of conc. acid leaked into sawdust packing and caused a fire [1]. A similar incident was involved in a freight-plane crash [2]. Fuming acid, leaking from a cracked bottle, ignited a wooden truck [3]. A retrospective survey on nitric acid packed in sawdust reveals an incident before 1894 [4].
See other PACKAGING INCIDENTS

Zinc ethoxide
See Zinc ethoxide: Nitric acid
See other INORGANIC ACIDS, OXIDANTS

4431. Peroxonitric acid

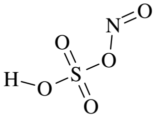
[26604-66-0] **HNO_4**



1. Schwarz, R., *Z. Anorg. Chem.*, 1948, **256**, 3
2. Kenley, R. A. *et al., J. Amer. Chem. Soc.*, 1981, **103**, 2205

The pure peroxoacid, prepared at —80°C, decomposes explosively at —30°C. Solutions in acetic acid or water of below the limiting concentration (corresponding to a stoicheiometric mixture of 70% aqueous nitric acid and 100% hydrogen peroxide) are stable, while those above the limit decompose autocatalytically, eventually exploding [1]. Explosion of the vapour when passed into a mass spectrometer inlet at 427°C (but not at 327°) was noted [2].
See other PEROXOACIDS

4432. Nitrosylsulfuric acid
[7782-78-7] **HNO_5S**



6-Chloro-2,4-dinitroaniline

See 2-Chloro-4,6-dinitroaniline: Nitrosylsulfuric acid

Dinitroaniline

Anon., *BCISC Quart. Safety Summ.*, 1970, **41**, 28

During plant-scale diazotisation of a dinitroaniline hydrochloride, local increase in temperature, owing to high concentration of the reaction mixture, caused a violent explosion.

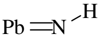
See Nitric acid: 4-Chloro-2-nitroaniline

See other INORGANIC ACIDS, NITROSO COMPOUNDS, OXIDANTS

Preparative hazard

See Nitric acid: Sulfur dioxide

4433. Lead(II) imide
[12397-26-1] **HNPb**



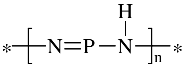
Alone, or Acids, or Water

Mellor, 1940, Vol. 8, 265

It explodes on heating, or in contact with water or dilute acids.

See other N-METAL DERIVATIVES

4434. Phospham
[22722-08-3] **HN_2P**



Hydrogen sulfide

Mellor, 1940, Vol. 8, 270

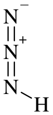
The solid produced by interaction of phospham and hydrogen sulfide at red heat is probably a trimeric triphosphatriazine such as phospham. The solid ignites in slightly warm air or in dinitrogen tetraoxide, and is violently oxidised by nitric acid.

Oxidants

Mellor, 1940, Vol. 8, 269—270

Interaction with copper(II) oxide or mercury(II) oxide proceeds incandescently. Mixtures with a chlorate or nitrate explode on heating. Phospham ignites in dinitrogen tetraoxide.
See related NON-METAL HYDRIDES

4435. Hydrogen azide (Hydrazoic acid)
[7782-79-8] **HN_3**



1. Smith, 1966, Vol. 2, 214
2. Bowden, F. P. *et al., Endeavour*, 1962, **21**, 121
3. Audreith, L. F. *et al., Inorg. Synth.*, 1939, **1**, 77
4. Kemp, M. D., *J. Chem. Educ.*, 1960, **37**, 142
5. Birkofer, L. *et al., Org. Synth.*, 1970, **50**, 109
6. Shapiro, E. L., *Chem. Eng. News*, 1974, **52**(2), 5
7. Chandross, E. A. and Gunderson, H., *Chem. Eng. News*, 1974, **52**(24), 5
8. Sood, R. K. *et al., J. Therm. Anal.*, 1981, **20**, 491—493

Hydrogen azide is quite safe in dilute solution, but is violently explosive and of variable sensitivity in the concentrated (17—50%) or pure states. Wherever possible, a low-boiling solvent (ether, pentane) should be added to its solutions to prevent inadvertent concentration by evaporation and recondensation. If this is not possible, no unwetted part of apparatus containing its solutions should be kept at a temperature appreciably below the boiling point (35°C) of the pure acid. The pure acid has often been isolated by distillation, but appears to undergo rapid sensitisation on standing, so that after an hour, faint vibrations or speech are enough to initiate detonation [1]. The solid acid (—80°C) is also very unstable [2]. Preparative procedures have been detailed [3]. It is readily formed on contact of hydrazine or its salts with nitrous acid or salts thereof. A safe procedure for the preparation of virtually anhydrous hydrogen azide has been described [4]. Trimethylsilyl azide serves as a safer and stabler substitute for hydrogen azide in many cases [5]. A laboratory explosion [6] seems likely to have been caused by the use of a huge (90-fold) excess of azide in too-concentrated solution and at too low an ambient temperature, leading to condensation of highly concentrated hydrogen azide. This penetrated into a ground-glass joint, and explosion was initiated on removing the stopper [7]. It is claimed that it may be distilled without fear of explosion if the trapping of the liquid azide in ground joints is prevented by thorough pregreasing of all joints [8].

As the lowest MW azide, hydrogen azide is extremely endothermic (ΔH_f° (g) +294.1 kJ/mol, 6.83 kJ/g).
See Methyl azide
See also 4-Chlorophenyl isocyanate
See also Nitrous acid: A semicarbazone, etc.
See other ENDOTHERMIC COMPOUNDS, INORGANIC ACIDS, NON-METAL AZIDES
See other GLASS INCIDENTS

Heavy metals

1. Napier, D. H., private comm., 1972
2. Cowley, B. R. *et al., Chem. & Ind.*, 1973, 444
3. Mellor, 1967, Vol. 8, Suppl. 2, 4

Great care is necessary to prevent formation of explosive heavy metal azides from unsuspected contact of hydrogen azide with heavy metals. Interaction of hydrazine and nitrite salts in a copper drainage system caused formation and explosion of copper azide deposits [1]. Use of a brass water-pump and vacuum gauge during removal of excess hydrogen azide under vacuum formed deposits which exploded when the pump and gauge were handled later [2]. Raney nickel catalyses the vigorous decomposition of solutions of hydrogen azide [3].

See Cadmium azide (reference 2), Sodium azide: Heavy metals

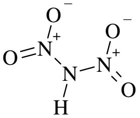
Oxidants

Vij, A. *et al., J. Amer. Chem. Soc.*, 2001, **123**(26), 6308

Condensing hydrazoic acid into Teflon tubes, with oxidants, at liquid nitrogen temperatures, frequently gave explosions during condensation or melting.

4436. Dinitramine (Dinitramide) (Nitronitramide)

[114045-20-4] **HN_3O_4**



1. Borman, S., *Chem. Eng. News*, 1994, **72**(3), 18
2. Dawe, J. R. *et al., Proc. Int. Pyrotech. Semin.*, 1998, **24th**, 789
3. Sjoeberg, P. *Theor. & Computational Chem.*, 2003, **12**, 389

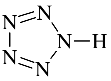
Salts of the acidic dinitramine find use as oxidants in propellant formulations. The dinitramine itself is explosively unstable, though more stable than nitramide [1]. Although described as relatively stable the sodium salt has an autoignition temperature of 123°C, the potassium 140°C [2]. An extensive discussion of dinitramine, its salts (especially the ammonium salt) and applications has appeared [3].

See Nitric amide

See other N—NITRO COMPOUNDS

4437. Pentazole

[289-19-0] **HN_5**

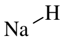


1. Sorbe, 1968, 140
2. Butler, R. N. *et al., J. Chem. Soc, Chem. Comm.*, 2003, (8), 1016

Pentazole (98.7% nitrogen) and its compounds are explosive [1]. Most such compounds claimed seem actually to have been azides, but still explosive. The first authentic preparation, but not isolation, of pentazole and pentazolides, in solution, is claimed much later [2]. Only arylpentazoles have been isolated and characterised, they, too, are explosive.
See other HIGH-NITROGEN COMPOUNDS
See related TETRAZOLES

4438. Sodium hydride

[7646-69-7] **HNa**



1. Plesek, J. *et al., Sodium hydride* (Engl. transl., Jones, G.) 5, 8, London, Iliffe, 1968
2. Bigou, F., personal communication, 1993
3. Gibb, T. R. P., US Pat. 2 702 281, 1955
4. Urben, P. G., personal experience

Commercial sodium hydride may contain traces of sodium which render it spontaneously flammable in moist air, or air enriched with carbon dioxide. The very finely divided dry powder ignites in dry air. Dispersions of the hydride in mineral oil are safe to handle. All normal extinguishers are unsuitable for solid sodium hydride fires: powdered sand, ashes or sodium chloride are suitable [1]. Commercial oil-coated sodium hydride was washed with dichloromethane to remove the oil. During later charging to a reactor containing more dichloromethane and an involatile substrate the hydride ignited. Ignition was probably by traces of moisture, but combustion seems to have continued in an atmosphere of hydrogen and dichloromethane vapour. It seems inadvisable to mix sodium hydride with most chlorinated solvents. Although a protective coating of non-hydridic material may prevent immediate reaction, it is thermodynamically capable of reacting energetically with halocarbons [2].

Many acylation reactions of esters using sodium hydride as base appear autocatalytic, with considerable potential for runaway, since the active base in solution is an alkoxide and the alcohol is a product of reaction [4]. A safe form of sodium hydride (as a solid solution in a halide) for large-scale industrial use has been claimed [3].
See Sodium: Halocarbons

Acetylene
Mellor, 1940, Vol. 2, 483
Dry acetylene does not react with sodium hydride below 42°C, but in presence of moisture, reaction is vigorous even at —60°C.

Diethyl succinate, Ethyl trifluoroacetate
Harris, A. R. *et al., Chem. Brit.*, 1983, **19**, 645
Acylation of diethyl succinate by ethyl trifluoroacetate in presence of sodium hydride and in absence of a solvent is hazardous, fire or explosion occurring on 2 occasions some 10—20 min after adding a little of the succinate to the hydride—trifluoroacetate premixture at 60°C. Presence of a solvent appears to eliminate the hazard.
See Ethyl trifluoropropionate, below

Dimethyl sulfoxide

See Dimethyl sulfoxide: Sodium hydride

Dimethylformamide

1. Buckley, J. *et al., Chem. Eng. News*, 1982, **60**(28), 5
2. De Wall, G. *Chem. Eng. News*, 1982, **60**(37), 5, 43

A mixture of the hydride and solvent was heated to, and held at 50°C. An exothermic reaction, which increased the temperature to 75°C, could not be controlled by external cooling, and the pilot-scale reactor contents erupted. It was later found that an exotherm began to develop at 26° (or at 40—50° with carefully dried solvent), and the subsequent reaction accelerated rapidly. Avoidance of holding mixtures hot is recommended, particularly when scaling up reactions. Similar behaviour was seen with dimethylacetamide [1]. A further similar plant-scale incident was reported, with onset of the exotherm at 40°C, followed by self-heating to 100°C in 10 min, even with maximum cooling applied [2].

See other SELF-ACCELERATING REACTIONS

Ethyl 2,2,3-trifluoropropionate

Bagnall, R. D., private comm., 1972

The ester decomposes violently in presence of sodium hydride, probably owing to hydride-induced elimination of hydrogen fluoride and subsequent exothermic polymerisation.

See Methyl trichloroacetate: Trimethylamine

Glycerol

Unpublished observations, 1956

Exothermic interaction of granular hydride with undiluted (viscous) glycerol with inadequate stirring caused charring to occur. Dilution with THF to reduce viscosity and improve mixing prevented local overheating during formation of monosodium glyceroxide.

Halogens MRH Chlorine 3.10/30

Mellor, 1940, Vol. 2, 483

Interaction with chlorine or fluorine is incandescent at ambient temperature, and with iodine at 100°C.

Other reactants

Yoshida, 1980, 215

MRH values calculated for 8 combinations with various materials are given.

Oxygen MRH 2.59/31

See Oxygen (Gas): Metal hydrides

Sulfur MRH 1.25/16

See Sulfur: Sodium hydride

Sulfur dioxide MRH 1.21/43

Moissan, H., *Compt. rend.*, 1902, **135**, 647

Sulfur dioxide reacts explosively in contact with sodium hydride unless diluted with hydrogen.

Water

1. Braidech, M. M., *J. Chem. Educ.*, 1967, **44**, 321
2. *MCA Case History No. 1587*

Addition of sodium hydride to a damp reactor which had not been purged with inert gas caused evolution of hydrogen and a violent explosion. Solid dispersions of the hydride in mineral oil are more easily and safely handled [1]. When an unprotected polythene bag containing the hydride was moved, some of the powder leaked from a hole, contacted moisture and immediately ignited. Such materials should be kept in tightly closed containers in an isolated, dry location [2].

See other GAS EVOLUTION INCIDENTS, METAL HYDRIDES, REDUCANTS

4439. Sodium hydroxide

[1310-73-2] **HNaO**

$$Na^{+} \qquad O{-}H$$

(*MCA SD-9*, 1968); *NSC 373*, 1982; *HCS 1980*, 845 (solid), 846 (33% solution); *RSC Lab. Hazards Safety Data Sheet No. 36*, 1985

Aluminium, Arsenical materials
See Aluminium: Arsenic trioxide, etc.

Ammonia, Silver nitrate
See Silver nitrate: Ammonia, Sodium hydroxide

1,4-Benzenediol
See 1,4-Benzenediol: Sodium hydroxide

N,N′-Bis(2,2,2-trinitroethyl)urea
See N,N′-Bis(2,2,2-trinitroethyl)urea: Sodium hydroxide

Bromine
See Bromine: Sodium hydroxide

4-Chloro-2-methylphenol
See 4-Chloro-2-methylphenol: Sodium hydroxide

4-Chlorobutyronitrile
See 4-Chlorobutyronitrile: Sodium hydroxide

Chloroform, Methanol MRH Chloroform 2.05/43
See Chloroform: Sodium hydroxide, etc.

Cinnamaldehyde
See Cinnamaldehyde: Sodium hydroxide

Cyanogen azide
See Cyanogen azide: Sodium hydroxide

Diborane
See Diborane: Octanal oxime, etc.

2,2-Dichloro-3,3-dimethylbutane

See 2,2-Dichloro-3,3-dimethylbutane: Sodium hydroxide

Esters, Water

1. Rowe, S., *Chilworth Technology Process Safety News*, 2001
2. Editor's comment 2001

A case is reported in which an ester hydrolysis did not initially proceed, and then ran away leading to boiling and vessel pressurisation. Liberated ethanol acted as a phase transfer catalyst [1]. Strong solutions of alkali (40% or more) show negligible mixing with most organic liquids and are often ineffective at ester hydrolysis, despite very good agitation. In some cases, even addition of water may be enough to initiate violent reaction [2].

Glycols

1. Cardillo, P. *et al., Chim. e Ind.* (Milan), 1982, **64**, 781—784
2. Gustin, J.-L., *Trans. Inst. Chem. Eng*, 2002, **80**(B), 16

Various mixtures of the base with ethylene glycol or diethylene glycol when heated in DSC capsules show exothermic decomposition around 230°C with rapid evolution of hydrogen. The exotherms increase with the base:glycol ratio, and the principal hazard arises from the rapid increase of pressure in closed systems caused by hydrogen evolution [1]. The sodium hydroxide/glycol reaction starts below 200°C given sufficiently long initiation period [2].

See Sodium 2-hydroxyethoxide

See entry GAS EVOLUTION INCIDENTS, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Maleic anhydride MRH 1.67/99+

See Maleic anhydride: Bases, etc.

4-Methyl-2-nitrophenol

See 4-Methyl-2-nitrophenol: Sodium hydroxide

3-Methyl-2-penten-4-yn-1-ol

See 3-Methyl-2-penten-4-yn-1-ol: Sodium hydroxide

Nitrobenzene

See Nitrobenzene: Alkali

Other reactants

Yoshida, 1980, 213

MRH values calculated for 12 combinations with various materials are given.

Sodium tetrahydroborate

See Sodium tetrahydroborate: Alkali

Succinic anhydride

See Succinic anhydride: Sodium hydroxide

Sugars

See SUGARS

1,2,4,5-Tetrachlorobenzene

See 1,2,4,5-tetrachlorobenzene: Sodium hydroxide, Solvent

12,2,2-Trichloroethanol

See 2,2,2-Trichloroethanol: Sodium hydroxide

Trichloroethylene MRH 2.26/45

See Trichloroethylene: Alkali

Trichloronitromethane MRH 1.80/46

See Trichloronitromethane: Sodium hydroxide

Water

1. *MCA SD-9*, 1968
2. *Haz. Chem. Data*, 1975, 267
3. *MCA Case History No. 2166*
4. Anon., *Loss Prev. Bull.*, 1987, (078), 26

The heat of solution is very high, and with limited amounts of water, violent boiling or even ignition of adjacent combustibles may occur [1,2]. The case history describes the disposal of open ended drums of waste caustic soda by putting into an empty hopper and sluicing out the solid alkali with a hot water jet. When the outlet became blocked, the hopper partly filled with hot water, and addition of a further drum caused a violent eruption to occur [3]. A tank holding 73% caustic soda solution at 121°C was found to be leaking and some of the contents were pumped out. A residue of 50 m^3 was to be diluted with water before removal and 100 m^3 of hot water was introduced via a hose into the top of the tank, where it formed a top layer. A compressed air lance was then introduced to mix the contents. After 30 min. a violent eruption occurred as the layers suddenly mixed to give a very large exotherm, and the steam so produced buckled the top of the tank [4].

See Potassium hydroxide: Water

Zinc

See Zinc: Sodium hydroxide

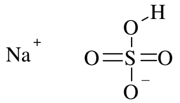
Zirconium

See Zirconium: Oxygen-containing compounds

See other INORGANIC BASES

4440. Sodium hydrogen sulfate

[7681-38-1] **$HNaO_4S$**



Acetic anhydride, Ethanol

See Acetic anydride: Ethanol etc.

Calcium hypochlorite

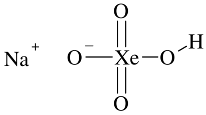
See Calcium hypochlorite: Sodium hydrogen sulfate

See other METAL OXONON-METALLATES

See related INORGANIC ACIDS

4441. Sodium hydrogen xenate

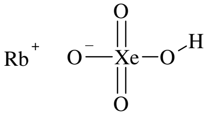
[73378-53-7], sesquihydrate **$HNaO_4Xe$**



See other XENON COMPOUNDS

4442. Rubidium hydrogen xenate

[73378-55-9], sesquihydrate **HO_4RbXe**



See other XENON COMPOUNDS

4443. 'Solid Phosphorus hydride'

[ ] **HP_2**

[3421]

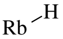
1. Mellor, 1940, Vol. 8, 851
2. Sidgwick, 1950, 730

This material (possibly phosphine adsorbed on phosphorus, and produced by decomposition of diphosphane in light) ignites in air, on impact, or on sudden heating to 100°C [1,2].

See other NON-METAL HYDRIDES

4444. Rubidium hydride

[13446-75-8] **HRb**



Acetylene

Mellor, 1940, Vol. 2, 483

In presence of moisture, interaction of the hydride and acetylene is vigorous at — 60°C, while in dry acetylene, reaction only occurs above 42°C.

Oxygen

See Oxygen (Gas): Metal hydrides

Water

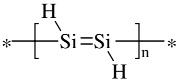
Mellor, 1963, Vol. 2, Suppl. 2.2, 2187

Interaction with water is too violent to permit of safe use of the hydride as a drying agent. When dispersed as a solid solution in a metal halide, it can be used as a drying or reducing agent.

See other METAL HYDRIDES

4445. Silicon monohydride (Silylidyne)

[13774-94-2] **$(HSi)_n$**



Alkali

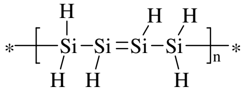
Stock, G. *et al., Angew. Chem.*, 1956, **68**, 213

The polymeric hydride is relatively stable to water, but reacts violently with alkali, evolving hydrogen.

See other NON-METAL HYDRIDES

4446. 'Unsaturated' Silicon hydride

[ ] **$(H_{1.5}Si)_n$**



Bailar, 1973, Vol. 1, 1350

The polymeric material (composition varies from $SiH_{1.42}$ to $SiH_{1.56}$) burns with a shower of sparks if heated in air.

See other NON-METAL HYDRIDES

†4447. Hydrogen (Gas)

[1333-74-0] **H_2**

H_2

FPA H20, 1974; *HCS 1980*, 544 (cylinder)

1. Pignot, A., *Chaleur Ind.*, 1939, **20**, 251—259
2. Anon., *Loss Prev. Bull.*, 1977, (015), 2
3. Fenning, R. W. *et al., Engineering*, 1930, **130**, 252
4. Messelt, W., *Engineering*, 1922, **113**, 502
5. Neer, M. E., *Diss. Abstr. Int. B*, 1972, **33**, 686

6. Carhart, H. W., *et al., AD Rep. No. 781862/1GA*, 1—39, Richmond (Va.), USNTIS, 1974
7. Neer, M. E., *Amer. Inst. Aero. Astron. Paper 74-1159*, 1974, 1—7
8. *NASA Tech. Memo. TMX-71565*, Richmond (Va.), USNTIS, 1971
9. Andrew, H. G., *School Sci. Rev.*, 1979, **61**(215), 292—294
10. Boeck, H., *Chem. Sich.*, 1982, **29**(4), 158—160
11. McCue, J. C., *Altern. Energ. Sources, 1980*, 1983, **3**, 419—427
12. Hydrogen Safety Manual, Balthasar, W. *et al.*, Luxembourg, Comm. Euro. Commun., 1983
13. Angus, H. C., *Chem. & Ind.*, 1984, 68—72
14. Lee, J. H. S. *et al., Adv. Heat Transfer*, 1997, **25**, 59

Several of the combustion-related properties of hydrogen in air, such as its wide flammability limits (4—75 vol%), wide detonation range (20—65 vol%), very low spark ignition energy (0.02 mJ), high heat of combustion (121 kJ/g) and high flame temperature (2050°C) combine to emphasise the high fire-related hazards of the lightest element. Sudden release of hydrogen into the atmosphere from storage at above 79 bar may cause spontaneous ignition, owing to the inverse Joule-Thompson effect [1]. This, however, does not always occur in practice, largely because of the low value of the effect (1.8°C/110 bar drop at 20°C; 3.9°/100 bar at 100°), so that ignition is unlikely unless the gas temperature is close to the auto-ignition temperature of 530—590°C [2] (or unless catalytic impurities are involved). Release of hydrogen at 47.5 bar into a vented 17.5 l chromium-plated sphere had caused explosive ignition [3]. Earlier, it had been found that a release of hydrogen for filling balloons would ignite under certain circumstances when the aperture was rusted, a brush discharge then being visible [4]. Spontaneous ignition of flowing hydrogen—air mixtures has been studied [5]. All aspects of hazards involved in the production, storage, handling and use of hydrogen as a Navy fuel are discussed [6]. In a study of the causes of auto-ignition of fast flowing hydrogen—air mixtures, at velocities above 750 m/s ignition occurred at temperatures 400°C below those established for static mixtures [7]. All recorded incidents and accidents involving hydrogen ignition have been reviewed and analysed [8]. Safety aspects of the generation and use of hydrogen in school demonstrations are detailed [9,10]. A compact portable ultrasafe storage unit for hydrogen for laboratory use has been developed, based on a lanthanum—nickel alloy hydride storage capsule, to eliminate hazards associated with use of high pressure storage of hydrogen [11]. A safety manual devoted to hydrogen has been published [12], and safety matters are included in a review of current technological aspects of storage, distribution and compression of hydrogen [13]. A detailed review of combustion and explosion properties of hydrogen, and of associated parameters, with a particular eye to nuclear reactor safety, has been published more recently [14].

Acetylene, Ethylene

Anon., *BCISC. Quart. Safety Summ.*, 1974, **45**, 2—3

In a plant producing 200 kt/a of ethylene from cracked naphtha, acetylene in the product was hydrogenated to ethylene in a catalytic unit operated under conditions mild enough not to hydrogenate ethylene. During a temporary shut-down and probably owing to operating error, the internal temperature in the catalytic unit rose to about 400°C, though the external wall temperature was recorded as excessive at 120°C. Attempts to reduce the temperature by passing in additional ethylene were unsuccessful, as the conditions were now severe enough to hydrogenate ethylene. This exothermic reaction increased the temperature, finally to 950°C, and the extensive cracking to methane, carbon and hydrogen now occurring was accompanied by further pressure increase. Plant failure was followed by an explosion and fire which took 4 days to extinguish, and damage totalled 6M sterling.

See other HYDROGENATION INCIDENTS

Air

1. Berman, M., *Nucl. Sci. Eng.*, 1986, **93**(4), 321—347
2. Edeskuty, F. J. *et al., Adv. Hydrogen Energy*, 1986, **5** (Hydrogen Energy Prog. 6, Vol. 1), 147—158
3. Cummings, J. C. *et al., Sandia Nat. Lab. Report, SAND-86-0173*, 1987, DE87011907 (USNTIS. Richmomd, Va)
4. Mottin, M. C., *Proc. 11th Int. Sympos. Prev. Occup. Risks Chem. Ind.*, 383—385, Heidelberg, ISSA, 1987
5. Vasil'ev, A. A. *et al., NATO Sci. Ser. 1*, 1999, **26**, 151

Large-scale experimental work indicates that transition of hydrogen—air mixtures from deflagration to detonation is considerably affected by geometrical factors and scale, and that transition to detonation may be rather more likely in large-scale incidents than previously supposed [1]. Safety aspects of large-scale combustion of hydrogen—air mixtures, especially in confined volumes, have been investigated [2]. Factors involved in the flame acceleration observed in combustion of hydrogen—air mixtures were investigated experimentally in closed and vented vessels, and the results cast doubt on the validity of existing explosion-venting guidelines [3]. Based on several accidents and on large-scale experimental investigations of unconfined explosions of hydrogen—air mixtures, it was concluded that 0.1% of the energy potentially available was effectively released [4]. An extensive study of detonation of hydrogen in air and with oxygen has been published [5].

Air, Catalysts

Mellor, 1942, Vol. 1, 325, 1937, Vol. 16, 146

Catalytically active platinum and similar metals containing adsorbed oxygen or hydrogen will heat and cause ignition in contact with hydrogen or air, respectively. Nitrogen purging before exposure to atmosphere will eliminate the possibility.

Air, Various vapours

Schumacher, H. J., *Angew. Chem.*, 1951, **63**, 560—561

The effects of the presence of 44 gaseous or volatile materials upon the upper explosion limits of hydrogen—air mixtures have been tabulated.

Benzene, Raney nickel catalyst

See Benzene: Hydrogen, Raney nickel

Calcium carbonate, Magnesium

See Magnesium: Calcium carbonate, Hydrogen

Carbon monoxide, Oxygen

See Oxygen: Carbon monoxide, Hydrogen

Catalyst

Bretherick, L., *CISHC Chem. Safety Summ.*, 1980, **51**, 111

Ignition of hydrogen leaking from a hydrogenation autoclave stirrer gland was attributed to traces of hydrogenation catalyst dust outside the reactor.

Catalyst, 3,4-Dichloronitrobenzene

See 3,4-Dichloronitrobenzene: Catalyst, Hydrogen

Catalysts, Vegetable oils

Smirnov, V. M., *Chem. Abs.*, 1938, **32**, 4368_6

Flash fires and explosions which frequently occurred on discharge of the hot products of catalytic hydrogenation of vegetable oils were attributed to formation of phosphine from the phosphatides present to a considerable extent in, e.g., rape-seed and linseed oils.

See other HYDROGENATION INCIDENTS

Ethylene, Nickel catalyst

Anon., *Loss Prev. Bull.*, 1977, (015), 4—5

Hydrogen from a naphtha cracker normally contains 10% of methane, practically no ethylene and a little carbon monoxide, and the latter is removed by passage over a heated nickel catalyst when it is hydrogenated to methane. Failure of the ethylene refrigeration compressor led to the presence of 8.5% of ethylene in the hydrogen. Presence of catalyst dust in the inlet tube caused rapid hydrogenation of ethylene to occur in this confined volume and the temperature rapidly increased. A temperature monitor set at 500°C also failed, and when the inlet tube reached 800°C it burst under the prevailing pressure and the hydrogen released immediately ignited. Preventive measures are detailed.

See other HYDROGENATION INCIDENTS

Halogens, or Interhalogens — MRH values show % of halogen

See Bromine: Hydrogen — MRH 0.45/99
Bromine fluoride: Hydrogen
Bromine trifluoride: Halogens, etc.
Chlorine trifluoride: Hydrogen-containing materials — MRH 6.82/97
Chlorine: Hydrogen — MRH 2.55/97
Fluorine: Hydrogen — MRH 13.39/95
Iodine heptafluoride: Carbon, etc.

Hydrogen peroxide, Palladium catalyst

See Hydrogen peroxide: Hydrogen, Palladium catalyst

Liquid nitrogen

1. Mel'nik, B. D. *et al., Chem Abs.*, 1963, **59**, 7309g
2. Bohlken, S. F., *Chem. Eng. Progr.*, 1961, **57**(4), 49—52

During the purification of washed hydrogen from cracking of natural gas, cooling with liquid nitrogen can lead to trapping of explosive products from interaction of alkenes in

the gas with oxides of nitrogen arising from biologically derived ammonium nitrate or nitrite in the scrubbing water. Various measures to prevent this are discussed. Similar effects may be observed when alkenes are oxidised in presence of nitrogen [1]. Analysis of a similar incident involving hydrogen derived from fuel oil implicated resins derived from interaction of nitrogen oxide (and possibly dinitrogen oxide) in a low-temperature heat exchanger section operating at —130 to —145°C [2].
See Nitrogen oxide: Dienes, Oxygen

Metals
Mellor, 1942, Vol. 1, 327
Lithium, calcium, barium and strontium react readily, sometimes igniting, in hydrogen above 300°C, while sodium and potassium react more slowly to form the hydrides.

Nickel, Oxygen
See Nickel: Hydrogen, Oxygen

2-Nitroanisole
See 2-Nitroanisole: Hydrogen

Oxidants
See Chlorine dioxide: Hydrogen
Copper(II) oxide: Hydrogen
Dichlorine oxide: Oxidisable materials
Difluorodiazene: Hydrogen
Dinitrogen oxide: Hydrogen, etc.
Dinitrogen tetraoxide: Hydrogen, etc.
Fluorine perchlorate: Hydrogen
Fluorine: Hydrogen, or: Hydrogen, Oxygen
Iodine heptafluoride: Carbon, etc.
Nitrogen oxide: Hydrogen, etc.
Nitryl fluoride: Non-metals
Oxygen (Gas): Hydrogen
Palladium(II) oxide: Hydrogen
Xenon hexafluoride: Hydrogen

Oxygen, Sulfuric acid
Tabata, Y. *et al., J. Haz. Mat.*, 1987, **17**, 47—59
Three PVC chlorine drying towers in a mercury amalgam cell chlorine plant suddenly exploded violently some time after the AC auxiliary power supply to the plant had failed, while the DC cell and brine feed supply had remained on. The failure of the pumped mercury circulation (and its flow alarm) through the electrolysis cells caused hydrogen (instead of sodium) to be liberated at the cathodes and oxygen at the anodes, so the chlorine gas output fed into the PVC drying towers trickle-fed with conc. sulfuric acid contained hydrogen and oxygen also. Ignition of the explosive mixture in the towers was caused by static sparks generated by the falling sulfuric acid drops: this was confirmed by a measurement of a static negative potential of 5kV inside and near the base of the towers. Other possible hazardous malfunctions in amalgam chlorine

cells and in non-conductive drying towers are described, and precautions to avoid such hazards discussed.
See other STATIC INITIATION INCIDENTS

Palladium trifluoride
See Palladium trifluoride: Hydrogen

Palladium, 2-Propanol
491M, 1975, 205
A stream of hydrogen containing entrained 2-propanol vapour and catalyst particles ignited in contact with air.
See HYDROGENATION CATALYSTS
See other HYDROGENATION INCIDENTS

Platinum catalyst
Dimitrov, I. *et al., Chem. Abs.*, 1981, **94**, 17876
Some characteristics of ignition of hydrogen on platinum catalyst (title only translated).

Poly(carbon monofluoride)
See Poly(carbon monofluoride): Hydrogen

1,1,1-Tris(azidomethyl)ethane, Palladium catalyst
See 1,1,1-Tris(azidomethyl)ethane: Hydrogen, etc.

Tris(hydroxymethyl)nitromethane
See Tris(hydroxymethyl)nitromethane: Hydrogen etc.
See other NON-METALS, REDUCANTS

4448. Hydrogen (Liquid)

1. Kit and Evered, 1960, 123
2. *Rept. UCRL-3072*, Univ. of California, Berkeley, 1955
3. Weintraub, A. A. *et al., Health Phys.*, 1962, **8**, 11
4. Edutsky, F. J., *Progr. Refrig. Sci. Technol., Proc. 12th Int. Congr. Refrig.*, 1969, **1**, 283—300
5. Lodini, M. A. K. *et al., Int. J. Hydrogen Energy*, 1989, **14**, 35—43
6. *NFPA 50B*, Quincy (Ma), Natl. Fire Prot. Assoc., 1989

The main precaution necessary for use of liquid hydrogen is to prevent air leaking into the system, where it will be condensed and solidified. Fracture of a crystal of solid air or oxygen could produce a spark to initiate explosion [1]. Procedures for the safe handling of liquid hydrogen in the laboratory [2] and in liquid hydrogen bubble chambers [3] have been detailed. Safety problems in large-scale handling and transport of liquid hydrogen have been discussed and safety codes described [4]. Sudden rupture of a 34 kl vacuum jacketed tank of liquid hydrogen appears to have been caused by accidental admission of air to the jacket space, causing excessive boil-off of gas beyond the capacity of the pressure relief [5]. A new US National Fire Code covers all aspects of construction, siting, piping, components and safety devices in consumer systems for liquid hydrogen [6].

Oxygen

1. Cai, T.-J., *Chem. Abs.*, 1981, **94**, 158861
2. Gamezo, V. N., *et al., Fizika Goreniya i Vzryva*, 1992, **28**(1), 106

Procedures to remove solid oxygen from liquefied hydrogen before storage are described [1]. Solid oxygen—liquid hydrogen mixtures are very detonable, with low critical diameters and anomalously high detonation velocities [2].

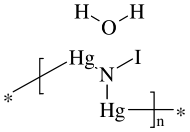
Ozone

See Ozone: Hydrogen (Liquid)

See other CRYOGENIC LIQUIDS

4449. Poly(dimercuryimmonium iodide hydrate)

[ ] **$(H_2Hg_2INO)_n$**



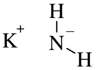
Sorbe, 1968, 97

It explodes on heating.

See other IODINE COMPOUNDS, POLY(DIMERCURYIMMONIUM) COMPOUNDS

4450. Potassium amide

[17242-52-3] **H_2KN**



1. Brandsma, 1971, 20—21
2. Sorbe, 1968, 68
3. Sanders, D. R., *Chem. Eng. News*, 1986, **64**(21), 2

It has similar properties to the much more widely used and investigated sodium amide, but may be expected on general grounds to be more violently reactive than the former. The frequent fires or explosions observed during work-up of reaction mixtures involving the amide were attributed to presence of unreacted (oxide-coated) particles of potassium in the amide solution in liquid ammonia. A safe filtration technique for removal of the particles is described [1]. It also ignites on heating or friction in air [2]. After preparation from liquid ammonia and potassium, the dry product after evaporation exploded while being chiselled out of the evaporator flask [3].

Ammonia, Copper(II) nitrate

See Copper(II) nitrate: Ammonia, Potassium amide

Potassium nitrite

See Potassium nitrite: Potassium amide

Tetraphenyllead

Houben-Weyl, 1975, Vol. 13.3, 241

One of the by-products of interaction is a highly explosive lead(IV) compound.

Water

Mellor, 1940, Vol. 8, 255

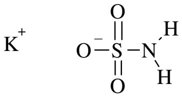
Interaction is violent and ignition may occur, even in contact with humid air. Old samples may explode with considerable delay after contact with water.

See Sodium amide: Water

See other N-METAL DERIVATIVES

4451. Potassium amidosulfate

[13823-50-2] **H_2KNO_3S**

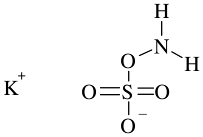


Metal nitrates or nitrites

See entry METAL AMIDOSULFATES

4452. Potassium hydroxylamine-*O*-sulfonate

[49559-20-8] **H_2KNO_4S**



1. Anon., private comm., 1985
2. Urben, P. G., private comm., 1989

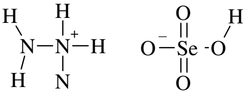
The salt was isolated (possibly as a hydrate) by unheated vacuum rotary evaporation. The stopper was later ejected from the flask by an exothermic decomposition. It was thought that the salt had been hydrolysed by the water of hydration to give potassium hydrogen sulfate and anhydrous hydroxylamine which is unstable at ambient temperature [1]. It seems more likely that the warm salt would undergo a bimolecular disproportionation to give potassium hydrogen sulfate and the *N*-amino derivative of the title compound, which would decompose to give more potassium hydrogen sulfate and the very reactive and unstable diazene. Hydroxylamine is now thought to be stable when pure [2].

See Diazene

See other N—O COMPOUNDS

4453. Potassium phosphinate (‘Potassium hypophosphite’)

[7782-87-8] **H_2KO_2P**



Air, or Nitric acid

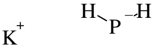
Mellor, 1940, Vol. 8, 882

The salt burns (owing to evolution of phosphine) when heated in air, and explodes when evaporated with nitric acid.

See other METAL PHOSPHINATES, REDOX REACTIONS, REDUCANTS

4454. Potassium dihydrogenphosphide

[13659-67-1] **H_2KP**



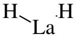
Mellor, 1971, Vol. 8, Suppl. 3, 283

The solid ignites in air.

See related PHOSPHINES

4455. Lanthanum dihydride

[13823-36-4] **H_2La**



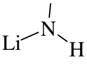
Kirk-Othmer, 1966, Vol. 11, 207

The very reactive hydride ignites in air.

See other METAL HYDRIDES

4456. Lithium amide

[7782-89-0] **H_2LiN**



Water

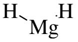
Bergstrom, F. W. *et al., Chem. Rev.*, 1933, **12**, 61

It reacts readily with water with a potentially dangerous exotherm.

See other N-METAL DERIVATIVES

4457. Magnesium hydride

[7693-27-8] **H_2Mg**



Air, or Water

1. Bailar, 1973, Vol. 1, 34—35
2. Ashby, E. C., *Inorg. Synth.*, 1977, **17**, 4
3. Anon., *Chem. Brit.*, 1985, **21**, 711
4. Vigeholm, B., *Chem. Abs.*, 1987, **106**, 165264

The finely divided hydride produced by pyrolysis is pyrophoric in air, while synthesis from the elements produces a substantially air-stable product [1]. That prepared by reduction of butylmagnesium bromide with lithium tetrahydroaluminate is pyrophoric and reacts violently with water and other protic compounds [2]. The hydride produced from magnesium anthracene has a very large specific surface area and is pyrophoric [3]. In the context of use of the hydride for energy storage purposes, ignition and combustion behaviour of 100—400 g portions were studied, as well as the reaction with water [4].

See other PYROPHORIC MATERIALS

Oxygen (Gas)

See Oxygen (Gas): Metal hydrides

See other METAL HYDRIDES

4458. Magnesium—nickel hydride

[67016-28-8] **$H_2Mg.H_2Ni$**

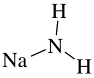
Hariguchi, S. *et al., Chem. Abs.*, 1981, **94**, 159191

Of several mixed hydrides, the magnesium—nickel hydrides were the most hazardous in terms of dust explosions.

See other DUST EXPLOSION INCIDENTS, METAL HYDRIDES

4459. Sodium amide

[7782-92-5] **H_2NNa**



FPA H102, 1981; *HCS 1980*, 826

1. Bergstrom, F. W. *et al., Chem. Rev.*, 1933, **12**, 61
2. Brauer, 1963, Vol. 1, 467
3. Krüger, G. R. *et al., Inorg. Synth.*, 1966, **8**, 15
4. Shreve, R. N. *et al., Ind. Eng. Chem.*, 1940, **32**, 173

5. Sandor, S., *Munkavédelem*, 1960, **6**(4—6), 20
6. Rüst, 1948, 283
7. Anon., *Univ. Safety Assoc. Safety News*, 1977, (8), 16
8. Ullmann, 1993, **A24**, 272

It frequently ignites or explodes on heating or grinding in air, particularly if previously exposed to air or moisture to produce degradation products (possibly peroxidic) [1,2,3]. Only one explosion not involving exposure to air has been recorded, during pulverisation [4]. The following oxidation products, all explosively unstable, have been identified: sodium hyponitrite, sodium trioxodinitrate, sodium tetraoxodinitrate, sodium pentaoxodinitrate and sodium hexaoxodinitrate [5]. Several cases of explosive incidents during packing or use of air-exposed material are described [6]. When a half-used 500 g bottle of sodamide was opened, sparks, fumes and intense heat were produced, leading to collapse of the bottle with subsequent explosion [7]. A test for safety of use consists of burning a gram on a spoon, if there are crepitations it is unsafe to use and should be cautiously destroyed [8].

Aryl halide, 1-Alkoxy-1-(trimethylsilyloxy)alkenes

Ferguson, J. R. *et al., Chem. Brit.*, 1997, **33**(6), 21

A mixture of sodamide, bromoanisole, and 1-methoxy-2-methyl-1-(trimethylsilyloxy)-1-butene were reacted at room temperature at a 50 millimolar scale. After some two hours, with slight emission of ammonia, the reaction suddenly became exothermic, with violent gas emission and on one occasion a fire. This was a modest scale-up of a literature procedure for synthesis of 2-alkylbenzoic acids, via a benzyne intermediate. It is advised that this reaction be employed only on smaller scale, with safety precautions. The reaction must pass through a benzocyclobutane intermediate, this, or another, high energy species might accumulate and then decompose.

Halocarbons MRH Carbon tetrachloride 3.31/50

Sorbe, 1968, 85

Interaction is explosively violent.

Other reactants

Yoshida, 1980, 264

MRH values calculated for 14 combinations with various materials are given.

Oxidants MRH values show % of oxidant

See Chromium trioxide: Sodium amide
Dinitrogen tetraoxide: Sodium amide MRH 4.31/48
Potassium chlorate: Sodium amide MRH 2.64/76
Sodium nitrite: Sodium amide

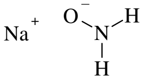
Water

1. Mellor, 1940, Vol. 2, 255
2. L Bretherick, Personal experience

Fresh material behaves like sodium with water, hissing, forming a diminishing floating globule, and often finally exploding [1]. Old, degraded (yellow) samples

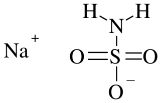
may be immersed in water for appreciable periods with little action, and then explode very violently. Disposal by controlled burning is safer [2].
See other N-METAL DERIVATIVES

4460. Sodium *O*-hydroxylamide
[22755-22-2] **H_2NNaO**



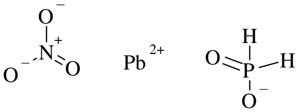
See Hydroxylamine: Metals

4461. Sodium amidosulfate
[13845-18-6] **H_2NNaO_3S**



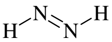
Metal nitrates or nitrites
See entry METAL AMIDOSULFATES

4462. Lead(II) nitrate phosphinate
[ ] **H_2NO_5PPb**



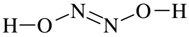
Bailar, 1973, Vol. 2, 131
It is powerfully explosive.
See other HEAVY METAL DERIVATIVES, REDOX COMPOUNDS

4463. Diazene
[3618-05-1] **H_2N_2**



Its extreme instability is matched by its extremely high endothermicity (ΔH_f° (g) +212.1 kJ/mol, 7.07 kJ/g)
See Potassium hydroxylamine-*O*-sulfonate (reference 2)
See other ENDOTHERMIC COMPOUNDS

4464. Hyponitrous acid
[14448-38-5] **$H_2N_2O_2$**



Alone, or Potassium hydroxide

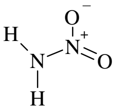
1. Sidgwick, 1950, 693
2. Mellor, 1940, Vol. 8, 407

An extraordinarily explosive solid, of which the sodium salt also explodes on heating to 260°C [1]. An attempt to prepare the acid by treating its silver salt with hydrogen sulfide caused explosive decomposition. Contact with solid potassium hydroxide caused ignition [2].

See Lead hyponitrite

See other N—O COMPOUNDS, REDUCANTS

4465. Nitric amide (Nitramide) (Nitramine)
[7782-94-7] **$H_2N_2O_2$**



Canis, C., *Rev. Chim. Minerale*, 1964, **1**, 521

Nitramide is quite unstable and various reactions in which it is formed are violent. Attempts to prepare it by interaction of various nitrates and sulfamates showed that the reactions became explosive at specific temperatures.

Alkalies

Thiele, J. *et al., Ber.*, 1894, **27**, 1909

A drop of conc. alkali solution added to solid nitramide causes a flame and explosive decomposition.

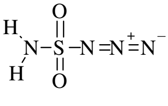
Sulfuric acid

Urbanski, 1967, Vol. 3, 16

Nitramide decomposes explosively on contact with conc. sulfuric acid.

See other N-NITRO COMPOUNDS

4466. Sulfamoyl azide (Amidosulfuryl azide)
[13449-16-6] **$H_2N_4O_2S$**



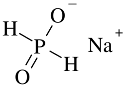
Shozda, R. J. *et al., J. Org. Chem.*, 1967, **32**, 2876

It is a low-melting solid, as shock-sensitive as glyceryl nitrate.

See other ACYL AZIDES

4467. Sodium phosphinate (‘Sodium hypophosphite’)

[7681-53-0] **H_2NaO_2P**



Mellor, 1940, Vol. 8, 881
Evaporation of aqueous solutions by heating may cause an explosion, phosphine being evolved.

Other reactants
Yoshida, 1980, 345
MRH values calculated for 6 combinations, largely with oxidants, are given.

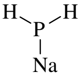
Oxidants MRH Sodium chlorate 2.88/49, sodium nitrate 1.00/44

1. Costa, R. L., *Chem. Eng. News*, 1947, **25**, 3177
2. Mellor, 1940, Vol. 8, 881
3. Mellor, 1971, Vol. 8, Suppl. 3, 624
4. Merck, 1996, 8775

Evaporation of a moist mixture of sodium phosphinate with a trace of sodium chlorate by slow heating caused a violent explosion. It was concluded that, once started, the decomposition of the phosphinate proceeds spontaneously [1]. Similar reactions have been reported with nitrates instead of chlorates. Such mixtures had previously been proposed as explosives [2]. It is reported that trituration of the hypophosphite with chlorates and other oxidants causes explosion [4]. Interaction of iodine with the anhydrous salt is violently exothermic, causing ignition [3].
See Perchloric acid: Sodium phosphinate
See other METAL PHOSPHINATES, REDOX REACTIONS, REDUCANTS

4468. Sodium dihydrogen phosphide

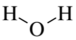
[24167-76-8] **H_2NaP**



Albers, H. *et al., Ber.*, 1943, **76**, 23
It ignites in air.
See related PHOSPHINES

4469. Diprotium monoxide (Water)

[7732-18-5] **H_2O**



1. Carson, P. J. *et al., Loss Prev. Bull.*, 1992, **102**, 7
2. Anon. *Safety Digest Univ. Safety Assoc.*, 1994, (50), 22 & 25
3. Editor’s comments, 1999

An extremely reactive liquid, solid or vapour with a dangerously high thermal capacity in both liquid and vapour state. When heated, the commonest cause of mid-19th century industrial explosions; it also bursts containers on cooling to low ambient temperatures. Still a frequent cause of vapour explosions today. Reacts with many metals to give hydrogen, sometimes violently. With non-metals pyrophoric hydrides may result. Frequently initiates explosive reactions between other substances. Violent reactions with many non-metal and some metal halides and oxyhalides, also with many organometallic compounds. Many metal nonmetallides produce toxic, flammable or pyrophoric gases on contact with diprotium monoxide.

The oxide interacts exothermically with strong acids and bases. When heated to decomposition, diprotium monoxide evolves the dangerous materials hydrogen, oxygen and hydrogen peroxide (all have individual entries in this Handbook). Passage of an electric current generates exactly that mixture of hydrogen and oxygen of maximal explosion risk. The same is true of ionising radiation and ultrasound, though in these instances some of the oxygen is initially held in solution as hydrogen peroxide, itself explosive. For a few incidents involving diprotium monoxide reactions see [1]. An opposed pair of explosions from careless handling of diprotium monoxide are reported. A student cooled some glass bottles of impure material in liquid nitrogen, they exploded surprisingly violently, causing lacerations. A technician removed a heated carboy of the pure material from an autoclave, a few seconds later it exploded (having presumably been superheated) causing severe burns (these were lessened because she was not wearing safety type footwear, which might have filled with the hot liquid, but open shoes able to drain) [2]. The editor has known injury result from safety footwear when diprotium monoxide at only 70°C ran into it. He has himself emerged almost unscathed in sandals when it was poured on his ankle at 100°C; a similar accident to a colleague wearing shoes immobilised the victim for a week. Reading those Internet sites which cover chemical safety, anecdotally, it is apparent that diprotium monoxide is almost level with nitric acid as a cause of memorable mishap, usually by contact with unsuspected metal or metal hydride traces, sometimes as a catalyst to solid mixtures of an oxidant and a reductant, and occasionally through explosive boiling when heated . In terms of human deaths caused, the most deadly material in this Handbook, also the initiator of the single chemical accident with the highest death toll. Too many potential cross-references to list.
See Deuterium oxide
See Methyl isocyanate

Aluminium, Sodium dithionite

Kirschner, E., *Chem. Eng. News*, 1995, **73**(18), 6

During attempts to clear a blocked benzaldehyde pipe, water was allowed to flow into a vessel containing 400 kg of aluminium powder and 2,500 kg of ‘sodium hydrosulfite’. The water reacted slowly with the hydrosulfite, evolving heat and hydrogen sulfide. Little attempt was made to deal with the reaction for 10 h. About 2 h later there was an explosion and fire, killing four operators who were attempting to nitrogen blanket the reactor. This was attributed to the aluminium having attained a temperature to react (in which case nitrogen would be useless, since air is unlikely to have been involved).
See Aluminium, Sodium dithionite

Electricity

Kondo, Y., *Chem Abs.*, 2000, **132**, 351907h

A hydrogen explosion consequent upon electrical corrosion protection of a boiler is reported. [Hydrogen is the product of unimpeded corrosion – electrolysis will give you mixed hydrogen and oxygen, which is still more hazardous].

Explosives and explosive mixtures

Yoshida, T. et al., *Safety of Reactive Chemicals & Pyrotechnics*, p105, Amsterdam, Elsevier, 1995

Although commonly believed to be a desensitiser of explosives, low percentage levels (up to 25%) of diprotium monoxide may have converse effects, increasing both sensitivity and power. There are explosives regularly initiated by it, and others may be if previously subjected to mechanical or thermal stress ,5]

See also CELLULOSE NITRATE

See also Sodium *aci*-nitromethanide

Incinerator dust

Takatsuki, H., *Chem. Abs.*, 1995, 122, 168826k

Evolution of hydrogen, attributed to presence of aluminium particles, formed an explosive atmosphere over wetted incinerator residues.

Metals

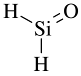
U.S. Dept of Energy, 1994, HDBK-1081-94, (*Spontaneous Heating and Pyrophoricity*), 51

Several incidents in which moisture has contributed to fires or explosions, in some of which water was definitely the sole oxidant, in zirconium, magnesium, uranium and thorium scraps or powders are retailed, largely sourced from an earlier paper. However, a plutonium fire was extinguished with water.

See also WATER-REACTIVE COMPOUNDS

4470. Oxosilane

[22755-01-7] **H_2OSi**



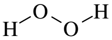
Kautsky, K., *Z. Anorg. Chem.*, 1921, **117**, 209

It ignites in air.

See related SILANES

4471. Hydrogen peroxide

[7722-84-1] **H_2O_2**



(*MCA SD-53*, 1969); *FPA H3*, 1972; *HCS 1980*, 549 (50%), 550 (30%), 551 (10%); *RSC Lab. Hazard Safety Data Sheet No. 57*, 1987

1. Shanley, E. S. *et al., Ind. Eng. Chem.*, 1947, **39**, 1536
2. Naistat, S. S. *et al., Chem. Eng. Progr.*, 1961, **57**(8), 76
3. Kirk-Othmer, 1966, Vol. 11, 407; *MCA SD-53*, 1969
4. Anon., *Fire Prot. Ass. J.*, 1954, 215
5. Smith, I. C. P., private comm., 1973
6. *MCA Case History No. 1121*
7. McClure, J. D., *J. Org. Chem.*, 1962, **27**, 627
8. Campbell, G. A. *et al., Proc. 4th Symp. Chem Process Haz. Ref. Plant* Des., 37—43, London, IChE, 1972
9. Clark, M. C. *et al., Chem. & Ind.*, 1974, 113
10. Cookson, P. G. *et al., J. Organomet. Chem.*, 1975, **99**, C31—32
11. *Manufacture of Organic Chemicals using Hydrogen Peroxide and Related* Compounds, AO 1.2, Widnes, Interox Chemicals Ltd., 1979
12. Berthold, W. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Chem.* Ind., 1431—1434, Basle, SSCI, 1980
13. Clemens, D., *Chem. Eng. News*, 1986, **64**(50), 2
14. Manning, D., *Chem. Eng. News*, 1987, **65**(9), 4
15. Merrifield, 1988, 23 pp.
16. *'Hydrogen Peroxide in Organic Chemistry'*, Schirmann, J. P., Delavarenne, S. T., Paris, Informations Chimie, 1987 (English edn.)
17. Ullmann, 1989, **A13**, 462
18. Mackenzie, J., *Chem. Eng.*, 1990, **97**(6), 84
19. Tojo, G. INTERNET, 1997
20. Davies, A. G. *et al., J. Chem. Soc., Perkin Trans, 2*, 1981, 1512
21. Matsui, H. *et al., Anzen Kogaku*, 2002, **41**(2), 114
22. Horizon Special: What sank the Khursk? BBC2 TV, Aug. 8th, 2000
23. Anon., *Sichere Chemiearbeit*, 2001, **53**(11), 128

The hazards attendant upon use of conc. hydrogen peroxide solutions have been reviewed [1,2,3]. Salient points include:

Release of enough energy during catalytic decomposition of 65% peroxide to evaporate all water present and formed, and subsequent liability of ignition of combustible materials.

Most cellulosic materials contain enough trace-metal catalysts to cause spontaneous ignition with 90% peroxide.

Contamination of conc. peroxide causes possibility of explosion. Readily oxidisable materials, or alkaline substances containing heavy metals, may react violently.

Soluble fuels (acetone, ethanol, glycerol) will detonate on admixture with peroxide of over 30% concentration, the violence increasing with concentration.

Handling systems must exclude fittings of iron, brass, copper, Monel, and screwed joints caulked with red lead preparations.

Concentrated peroxide may decompose violently in contact with iron, copper chromium and most other metals and their salts, and dust (which frequently contains rust). Absolute cleanliness, suitable equipment (PVC, butyl or Neoprene rubber, Teflon) and personal protection are essential for safe handling [4].

During concentration under vacuum of aqueous [5] or of aqueous—alcoholic [6] solutions of hydrogen peroxide, violent explosions occurred when the concentration was sufficiently high (probably over 90%) [3]. It is possible to accidentally concentrate 30% hydrogen peroxide to explosion on a laboratory rotary evaporator [19]. A suspension of 90% hydrogen peroxide in dichloromethane is shock-sensitive [7]. Detonation of hydrogen peroxide vapour has been studied experimentally [8]. Explosion of a screw capped winchester of 35% peroxide solution after 2 years owing to internal pressure of liberated oxygen emphasises the need to date-label materials of limited stability, and to vent the container automatically by fitting a Bunsen valve or similar device [9]. It has been suggested that hazards in use and handling of concentrated hydrogen peroxide can be avoided by using the solid 2:1 complex of hydrogen peroxide with 1,4-diazabicyclo[2.2.2]octane. This is hygroscopic but supposedly stable for at least several months in storage, although it has been reported to decompose above 60°C [10]. The 1:1 complex, which is of considerably lower energy, has proved explosive, however [20].

A survey, with many references, of 14 classes of preparative reactions involving hydrogen peroxide or its derivatives emphasises safety aspects of the various procedures [11]. Following the decomposition of 100 l of 50% aqueous hydrogen peroxide which damaged the 630 l stainless vessel rated at 6 bar, the effect of added contaminants and variations in temperature and pH on the adiabatic decomposition was studied in a 1 l pressure vessel, where a final temperature of 310°C and a pressure around 200 bar were attained. Rust had little effect, but addition of a little ammonia (pH increased from 1.8 to 6.0) caused the induction period to fall dramatically, effectively from infinity to a few h at 40°C and a few min at 80°C. Addition of sodium hydroxide to pH 7.5 reduced the induction period at 24°C from infinity to about 4 min [12]. A half full aluminium tank contining 85 m^3 of 60% peroxide self-heated and gased to explosion in a factory making sodium percarbonate. The tank-residue proved alkaline, despite addition of phosphoric acid (an iron chelator) while trying to control the heating. It was concluded that sodium carbonate solution had sucked back into the peroxide, giving base-catalysed decomposition [23]. A tank car explosion of 30% peroxide, possibly caused by cupric chloride contamination, is reported [21].

Several 0.5—1 l bottles of an unspecified plastic containing 30% hydrogen peroxide which had been stored for over a year became brittle and developed cracks during normal handling operations. One bottle stored for more than 4 years broke into small fragments when squeezed by hand [13]. However, these bottles were undoubtedly of the wrong material, because storage of up to 54% hydrogen peroxide solutions in suitable plastic bottles with no signs of container deterioration is a well-established commercial practice [14]. A more recent report and review update and extend general information on storage and handling of the powerful oxidant. Considerable attention is paid to headspace explosions caused by decomposition in the presence of volatile fuels. It is calculated that during adiabatic decomposition of 90% peroxide solution, a temperature of 740°C could be attained, accompanied by the release of 5233 volumes of oxygen and steam [15]. Detonation limit diagrams for hydrogen peroxide vapours against liquid phase composition, temperature and pressure are given [17]. Each chapter of a monograph is devoted to a specific functional group, and the final chapter is concerned with safety aspects of the use of hydrogen peroxide as oxidant in mixtures with organic compounds [16].

Use of hydrogen peroxide as a mono-propellant in military applications has led to accident, copper and steel being common in these environments. A related accident having happened to a British submarine, it was suggested that the loss of the Russian Khursk was caused by a torpedo motor prematurely starting in an air-filled torpedo tube. With no water resistance to the propellor , the motor then raced to disintegration, rupturing the peroxide lines and tank. Contact with catalytic metals, fire in an oxygen enriched environment and finally explosion of warheads followed [22]. More or less this explanation seems to have been accepted.

See other INDUCTION PERIOD INCIDENTS

Acetal, Acetic acid

Ashley, J. N. *et al., Chem. & Ind.*, 1957, 702

An organic sulfur compound containing an acetal function had been oxidised to the sulfone with 30% hydrogen peroxide in acetic acid. After the liquor had been concentrated by vacuum distillation at 50—60°C, the residue exploded during handling. This was attributed to formation of the peroxide of the acetal (formally a *gem*-diether) or of the aldehyde formed by hydrolysis, but formation and explosion of peracetic acid seems a more likely explanation.

Acetaldehyde, Desiccants

Karnojitzky, V. J., *Chim. Ind.* (Paris), 1962, **88**, 235

Interaction gives the extremely explosive poly(ethylidene) peroxide, also formed on warming peroxidised diethyl ether.

Acetic acid

1. Grundmann, C. *et al., Ber.*, 1939, **69**, 1755
2. *491M*, 1975, 207

During preparation of peracetic acid, the temperature should not be too low to prevent reaction as the reagents are mixed, because reaction may begin later with explosive violence [1]. Heating well-diluted peroxide and acid will exothermically produce the acid which may explode at 110°C [2].

Acetic acid, 3-Thietanol

1. Dittmer, D. C. *et al., J. Org. Chem.*, 1961, **26**, 1324
2. Dittmer, D. C. *et al., J. Org. Chem.*, 1971, **36**, 1324
3. Chang, P. *et al., J. Org. Chem.*, 1969, **34**, 2791
4. Lamm, B. *et al., Acta Chem. Scand. Ser. B*, 1974, **28**, 701—703

When following the original route [1] to 3-hydroxythietane-1,1-dioxide, it is essential to dilute and evaporate the hydrogen peroxide—acetic acid reaction mixture slowly from a large dish, to prevent explosions arising from concentration of peroxyacetic acid [2]. Alternative routes to avoid this hazard are available [3,4].

See Peroxyacetic acid

Acetic acid, Jute

De Forest, P. *et al., Chem. Eng. News*, 1987, **65**(31), 2; *J. Chem. Educ.*, 1988, **65**(8), 728—729

Jute fibre (0.1 g) was being prepared for a standard forensic examination by treatment in glacial acetic acid (20 ml) with hydrogen peroxide solution (20 ml, but in error 30% peroxide was used in place of the specified 6% '20-vol') strength. After heating on a water bath for 4 h, there was a violent explosion which shattered the ceramic hotplate below the bath with formation of 'ceramic shrapnel'. The available hydrogen peroxide would lead to formation of 14.7 g of peracetic acid as a 34 wt% solution in aqueous 33% acetic acid. This would be expected to become more concentrated by evaporation during prolonged heating, and concentrated solutions are known to be thermally unstable.

See Perchloric acid: Clay

Acetic acid, *N*-Heterocycles

1. Wommack, J. B., *Chem. Eng. News*, 1977, **55**(50), 5
2. Dholakia, S. *et al., Chem. & Ind.*, 1977, 963
3. Daisley, R. W. *et al., Org. Prep. Proc. Int.*, 1983, **15**, 281

During isolation of the di-*N*-oxide of 2,5-dimethylpyrazine [1] and of the mono-*N*-oxide of 2,2-bipyridyl [1], prepared by action of hydrogen peroxide in acetic acid on the heterocycles, violent explosions occurred on evaporation of the excess peroxyacetic acid. In the preparation of 3-bromopyridine *N*-oxide, the necessity to take adequate precautions against the possibility of explosion while vacuum distilling off excess reagents from a water bath maintained at 50°C is stressed [3]. For a method not involving this considerable explosion risk,

See 3-Methyl-4-nitropyridine *N*-oxide

See N-OXIDES

Acetic anhydride

1. Prett, K., *Textilveredlung*, 1966, **1**, 288—290
2. Swern, D., *Chem. Rev.*, 1945, **45**, 5

During preparation of peracetic acid solutions for textile bleaching operations, the reaction mixture must be kept acid. Under alkaline conditions, highly explosive diacetyl peroxide separates from solution [1]. An excess of the anhydride has the same effect [2].

Acetone, Other reagents MRH Acetone 6.36/19

1. Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 3
2. *MCA Case History No. 233*
3. *MCA Case History No. 223*
4. Stirling, C. J. M., *Chem. Brit.*, 1969, **5**, 36
5. Seidl, H. *Angew. Chem. (Intern. Ed.)*, 1964, **3**, 640
6. Treibs, W., *Angew. Chem. (Intern. Ed.)*, 1963, **3**, 802
7. Brewer, A. D., *Chem. Brit.*, 1975, **11**, 335
8. Schurz, J. *et al., Angew. Chem.*, 1956, **68**, 182
9. Ghilardi, C. A. *et al., J. Chem. Soc., Dalton Trans.*, 1986, 12075—2081
10. Anon., *Sichere Chemiearb.*, 1987, **39**, 70
11. Ullmann, 1989, **A13**, 462

Acetone and hydrogen peroxide readily form explosive dimeric and trimeric cyclic peroxides, particularly during evaporation of the mixture. Many explosions have occurred during work-up of peroxide reactions run in acetone as solvent, including partial hydrolysis of a nitrile [1] and oxidation of 2,2-thiodiethanol [2] and of an unspecified material [3]. The reaction mixture from oxidation of a sulfide with hydrogen peroxide in acetone exploded violently during vacuum evaporation at 90°C. On another occasion, oxidation of a sulfide in acetone in presence of molybdate catalyst proceeded with explosive violence. A general warning against using acetone as a solvent for peroxide oxidations is given [4]. During the isolation of 1-tetralone, produced by oxidation of tetralin with hydrogen peroxide in acetone, a violent explosion occurred which was attributed to acetone peroxide [5]. The originator of the method later gave detailed instructions for a safe procedure, which feature the exclusion of mineral acids, even in traces [6].

During oxidation of an unspecified sulfur heterocycle in acetone with excess 35% hydrogen peroxide, a white solid separated during 3 days standing in a cool place. The solid (20 g) appeared to have been acetone peroxide, because it exploded with great violence during drying in a vacuum oven. The previous warning [4] on incompatibility of acetone and hydrogen peroxide was repeated [7]. A cyclic diketone was oxidised with alkaline peroxide in acetone solution and the product isolated by a solvent extraction procedure. During vacuum evaporation of the ethyl acetate extract, gassing was noted and the concentrate was treated twice with platinum catalyst to decompose excess hydrogen peroxide. After filtration and further vacuum evaporation, further gassing was noted and heating was discontinued, but the residue exploded [8]. This seems likely to have happened because the cyclic acetone peroxides, as dialkyl peroxides (and unlike hydroperoxides) would largely survive the catalytic decomposition treatment.

During the oxidation of the ligand tris(diphenylphosphinylethyl)amine with hydrogen peroxide in acetone to give tris(diphenylphosphonylethyl)amine, overheating must be avoided to prevent damaging explosions (of acetone peroxide). A Teflon beaker is recommended for the reaction [9]. A thiol was being oxidised in acetone to the disulfide with hydrogen peroxide. No product separated on standing, so the solution was concentrated to one fifth of its bulk in a rotary vacuum evaporator, and a white solid separated. During subsequent operations, the solid (trimeric acetone peroxide) exploded with great violence [10].

Detonation limit diagrams for hydrogen peroxide, water, acetone systems are given [11].

See 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane

See KETONE PEROXIDES

Aconitic acid

Anon., private communication, 1993

An attempt was made to convert aconitic acid (2 g) to isocitric acid using 25 ml. of 30% aqueous hydrogen peroxide, time and temperature unspecified. A crystalline product precipitated which exploded on grinding in a mortar.

1. *MCA SD-53*, 1969
2. Spengler, G. *et al., Brennst. Chem.*, 1965, **46**, 117
3. Heemskerk, A. H. *et al., Loss Prevention and Safety Promotion in the Process Industries*, Vol I, (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 411, Amsterdam, Elsevier, 1995

Homogeneous mixtures of concentrated peroxide with alcohols or other peroxide-miscible organic liquids are capable of detonation by shock or heat [1]. Furfuryl alcohol ignites in contact with 85% peroxide within 1 s [2]. Detonability limits of mixtures with 2-propanol have been measured. Approximately stoichiometric combinations of 50% hydrogen peroxide and the alcohol could be made to detonate, as could a wider range of mixtures with higher test peroxide [3].

See Oxygenated compounds, etc., below

Alcohols, Sulfuric acid.

1. Hedaya, E. *et al., Chem. Eng. News*, 1967, **45**(43), 73
2. Merrifield, 1988, 5—6, 16

During conversion of alcohols to hydroperoxides, the order of mixing of reagents is important. Addition of conc. acid to mixtures of an alcohol and conc. peroxide almost inevitably leads to explosion, particularly if the mixture is inhomogeneous and the alcohol is a solid [1]. In presence of concentrated acid, hydrogen peroxide forms peroxymonosulfuric acid (Caro's acid), especially if the rate of conversion of the alcohol is low. The peroxyacid is a very powerful and unstable oxidant, and its reactions are often violent. Thus in the hydrogen peroxide—sulfuric acid—alcohol ternary system, an autodetonation region may exist. This is shown in a triangular diagram for 2-propanol and *tert*-butanol [2].

See tert-Butanol, etc.; 2-Phenyl-1,1-dimethylethanol; 3,5-Dimethyl-3-hexanol, all below

Aluminium isopropoxide, Heavy metal salts

Ward, D. S., unpublished information, 1974

During preparation of an alumina catalyst, the isopropoxide was stirred with 6% hydrogen peroxide to generate a slurry of pseudo-boehmite alumina, to which was added a solution of heavy metal salts. The heating and foaming of the mixture was excessive and foam overflowed into a safety tray, then ignited. The incident was attributed to either spontaneous or static-induced ignition of the foam consisting of oxygen-rich bubbles in the isopropanol-containing liquid medium. The heavy metal salts would catalyse decomposition of the hydrogen peroxide and may also have been involved in the ignition process.

See Metals, etc., below

2-Amino-4-methyloxazole

Rapi, G. *et al., J. Chem. Soc., Chem. Comm.*, 1982, 1339—1340

Oxidative rearrangement of the oxazole to 4-hydroperoxy-5-hydroxy-4-methylimidazolidin-2-one in presence of iron(II) catalysts at ambient temperature may become explosive if not controlled effectively.

Ammonia

Matlow, S. L., *Chem. Eng. News*, 1990, **68**(30), 2

A sealed container of mixed 30% aqueous solution and aqueous ammonia exploded on storage, driving shards into a wall 18 m away.

See Oxygen(Gas): Ammonia and Oxygen(Liquid): Ammonia

Aromatic hydrocarbons, Trifluoroacetic acid MRH Toluene 6.62/15

Demo, N. C. *et al., Tetrahedron Lett.*, 1977, 1703—1704

A solution of 30% aqueous hydrogen peroxide in trifluoroacetic acid is useful for destructive oxidation of the aromatic ring in preference to the side chains as is usual with most oxidants. During work-up operations, the excess peroxide must be catalytically decomposed with manganese dioxide before removal of solvent to prevent explosions.

Azelaic acid, Sulfuric acid

Berkowitz, S., US Pat. 4 147 720, 1979

Conversion of the acid to diperoxyazelaic acid in hydrogen peroxide/sulfuric acid medium at 45—50°C was uncontrollably exothermic and led to explosion. Use of a peroxide/phosphoric acid medium gives a safe and effective conversion of C_6—C_{16} diacids to the diperoxy acids, though up to 5% of sulfuric acid is needed as catalyst for C_{12}—C_{16} acids.

See Carboxylic acids, below

Bases

Aqueous hydrogen peroxide is catalytically decomposed by even small quantities of relatively mild bases such as ammonia or sodium carbonate. This is a convenient way of generating oxygen, but also of bursting inadequately vented containers. Such decomposition has also been involved in several of the accidents during waste treatment with peroxide, giving oxygen-rich headspaces.

See Waste treatment, below

Benzene

Merrifield, 1988, 13

A triangular diagram shows the range of explosive mixtures in the hydrogen peroxide—benzene—water ternary system, and also includes data for various oxygenated water-soluble organic compounds.

See Oxygenated compounds, below

Benzenesulfonic anhydride

Fichter, F., *Helv. Chim. Acta*, 1924, **7**, 1072

Attempts to prepare benzeneperoxysulfonic acid by interaction of the anhydride and 90—95% peroxide led to explosively violent decomposition within a few s. When diluted with acetic acid, the reaction mixture soon began to decompose, leading to violent boiling. It was concluded that the peroxyacid is too unstable for more than transitory existence.

tert-Butanol, Sulfuric acid

Schenach, T. A., *Chem. Eng. News*, 1973, **51**(6), 39

Preparation of di-*tert*-butyl peroxide by addition of *tert*-butanol to 50% hydrogen peroxide—78% sulfuric acid (1:2 by wt) is a dangerously deceptive procedure. On the small scale, and with adequate cooling capacity it may be possible to prevent the initial stage (exothermic formation of *tert*-butyl hydroperoxide) getting out of control and initiating violent or explosive decomposition of the peroxide—peroxomonosulfuric acid mixture. This hazard diminishes as the reaction proceeds with consumption of hydrogen peroxide and dilution by the water of reaction. On the plant scale several severe explosions occurred, preceded only by a gradual temperature increase, during attempted process development work.
See Alcohols, above

Carbon MRH 6.19/15

1. Mellor, 1939, Vol. 1, 936—938
2. Schumb, 1955, 402, 478

The violent decomposition observed on adding charcoal to conc. hydrogen peroxide is mainly owing to catalysis by metallic impurities present and the active surface of the charcoal, rather than to direct oxidation of the carbon [1]. Charcoal mixed with a trace of manganese dioxide ignites immediately on contact with conc. peroxide [2].

Carboxylic acids MRH Formic acid 3.30/58

Kuchta, J. M. *et al., Rep. Invest. No. 5877*, Washington, US. Bur. Mines, 1961
Admixture produces peroxyacids, some of which are unstable and explosive. Aqueous peroxide solutions containing formic acid, acetic acid or tartaric acid above certain concentrations can be caused to detonate by a severe explosive shock.
See Azelaic acid, etc., above; Oxygenated compounds, etc., below
See PEROXYACIDS

Catalyst (unspecified)

1. Anon., *Sichere Chemiearb.*, 1979, **31**, 63
2. Merrifield, 1988, 16

Aqueous cyanide residues were being detoxified by treatment with a catalyst and then 50% peroxide solution to oxidise cyanide to cyanate at pH 10±0.5 at above 40°C. Apparently all the alkaline catalyst solution had not been completely drained from the 100 l dosing flask before the peroxide solution (28 kg) was charged. The latter solution began to decompose and this accelerated to explosion, destroying the flask [1]. In a continuous bleaching plant, a 200 l stainless dosing vessel, unrelieved except for a small overflow line, was connected directly to a supply of 35 wt% peroxide solution and to the bleaching process vessel. Back-contamination of the peroxide solution in the dosing vessel led to exothermic decomposition, and the evolved gases caused the vessel to pressure-burst [2].
See other GAS EVOLUTION INCIDENTS

Coal

Wood, C. R., *Fuel*, 1974, **53**, 220
Coal (72 mesh) slurried with hydrogen peroxide solution (30 wt%) reacts steadily on warming to 85°C, but if much pyrites is present, the oxidation may accelerate to a dangerous extent.
See other CATALYTIC IMPURITY INCIDENTS

Copper(II) chloride

Merrifield, 1988, 7

In a printed circuit board etching line using copper(II) chloride solution, 45 wt% hydrogen peroxide solution was used to recover the copper salts. The peroxide header tank became contaminated with trace amounts of the etching solution, and catalytic decomposition of the peroxide led to a pressure burst of the tank.

See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

Cotton waste

Merrifield, 1988, 6

Spillage of a weak (5%) aqueous peroxide solution onto cotton waste led, after some time, to ignition. This probably involved concentration of the peroxide by evaporation/absorption of the water, the heat insulating effect of the fibrous mass preventing heat loss as oxidation proceeded, and possibly the presence of trace metals in the waste promoting catalytic decomposition.

See Wood, below

Diethyl ether

Bruhl, J. W., *Ber.*, 1895, **28**, 2856—2857

Evaporation of an ethereal solution of hydrogen peroxide gave a residue of which a drop on a platinum spatula exploded weakly on exposure to flame. When the sample (1—2 g) was stirred with a glass rod (not fire polished), an extremely violent detonation occurred.

See ETHERS

See other GLASS INCIDENTS

3,5-Dimethyl-3-hexanol, Sulfuric acid

MCA Guide, 1972, 315

The alcohol was treated with 90% hydrogen peroxide and a trace of sulfuric acid at 0°C. While warming to ambient temperature overnight it exploded violently. Some 3,5-dihydroperoxide may have formed from autoxidation at the 5-position.

See Alcohols, etc., above

See also tert-Butanol, etc., above

See also 2-Methyl-1-phenyl-2-propanol, etc., below

Dimethylphenylarsine

Anon., *Lab. Accid. Higher Educ.*, item 8, Barking, HSE, 1987

During the preparation of the *As*-oxide in glassware by oxidation with hydrogen peroxide (conditions unknown), an explosion occurred, possibly due to presence of impurities.

See Dimethylphenylphosphine, next below

Dimethylphenylphosphine

Dennister, M. L. *et al., Inorg. Synth.*, 1977, **17**, 185

Oxidation of the phosphine to the oxide by adding its solution in ether to stirred 15% aqueous peroxide may become very violent if the rate of addition is too fast.

See Dimethylphenylarsine, next above

Diphenyl diselenide

Bloodworth, A. J., *et al., J. Chem. Soc., Perkin Trans. 1*, 1983, 471—473

Attempted thermal dehydration of benzeneseleninic acid, formed by oxidation of diphenyl diselenide with hydrogen peroxide, gave a solid which exploded at 53—55°C. The solid may have been the complex of the acid with hydrogen peroxide.

2-Ethoxyethanol, Polyacrylamide gel, Toluene

1. Darnall, D. W., *Chem. Eng. News*, 1978, **56**(47), 47
2. Shanley, E. S., *Chem. Eng. News*, 1979, **57**(21), 43

Polyacrylamide gels were dissolved in 30% peroxide solution and added to a scintillation mixture in 1:1 2-ethoxyethanol—toluene. After counting, the mixtures were bulked and evaporated intermittently with heat during a 4 week period, and the accumulated peroxidised residues eventually exploded violently [1]. A subsequent comment indicated that peroxidised materials may not necessarily have been formed, because solutions of organic materials in aqueous peroxide are themselves potentially explosive [2].

See Oxygenated compounds, below

Ethyl acetate

Schierwater, F.-W., *Jahresber.*, 1981, 77

Organic material was extracted from a sample with methanol, and after evaporation the small residue was refluxed with aqueous peroxide. Extraction with ethyl acetate, separation and evaporation gave a residue which was scarcely visible but which exploded violently when the flask was moved. Several peroxidic species, including methyl hydroperoxide, peroxyacetic acid or its ethyl ester, may have been involved.

See Ethyl acetate

Fatty acid

Merrifield, 1988, 7

In a continuous operation to bleach a fat-derived acid, the latter was stirred and treated at 80°C with a slow stream of 50 wt% hydrogen peroxide. Un-noticed failure of the agitator led to peroxide build-up, layer formation and eventual formation of an explosive mixture. When this passed into a centrifugal pump, it detonated.

See other AGITATION INCIDENTS

Formic acid, Metaboric acid

See Peroxyformic acid

Gadolinium hydroxide

Bogdanov, G. A. *et al., Chem. Abs.*, 1976, **85**, 52253

Interaction gives a hydrated basic peroxide which decomposes explosively at 80—90°C.

Gallium, Hydrochloric acid

Titze, H., *Mikrochem. Acta*, 1977, 480

During dissolution for analysis of 1—9 g samples of gallium in conc. hydrochloric acid containing small portions of 30% hydrogen peroxide solution, cooling may be necessary to prevent development of explosively violent reactions at higher temperatures.

Hexamethylenetetramine
See 1,6-Diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane

Hydroboration product of 2-methyl-2-propenyl tetrahydropyranyl ether
See TETRAHYDROPYRANYL ETHER DERIVATIVES

Hydrogen selenide
Mellor, 1939, Vol. 1, 941
Interaction is very fast.

Hydrogen, Palladium catalyst
Anon., *Jahresber.*, 1982, 65—66
In the cyclic anthraquinone process for preparing hydrogen peroxide, a hydrocarbon solution of a 2-alkylanthraquinone is catalytically reduced with hydrogen to the 9,10-diol, which is then air-oxidised to the quinone with formation of hydrogen peroxide. The latter is removed from the process solution by water washing and phase separation, and the process stream, now virtually free of peroxide is recycled to the reactor. Failure of the compressed air supply prevented the separation of the aqueous hydrogen peroxide from the hydrocarbon phase, and both layers were recycled into the process. Contact of the peroxide solution with the catalyst released oxygen, which mixed with hydrogen and was ignited by the catalyst. The initial explosion released some of the flammable process solution which ignited, and eventually some 70 m^3 of the latter was involved in a major fire, with a further explosion in the hydrogenation plant.
See other HYDROGENATION INCIDENTS

Immiscible organic liquids
Merrifield, 1988, 5
Emulsions formed from immiscible organic liquids in aqueous peroxide mixtures may behave in the same way as miscible organic liquids, but if the emulsion breaks and separation of the organic phase occurs, passage into an explosive region of the peroxide—water—organic liquid ternary system may occur, and this is potentially very dangerous.

Iron(II) sulfate, 2-Methylpyridine, Sulfuric acid
Mond. Div., ICI, private. comm., 1969
Addition of 30% peroxide and sulfuric acid to 2-methylpyridine and iron(II) sulfate caused a sudden exotherm, followed by a vapour phase explosion and ignition. Lack of stirring is thought to have caused local overheating, vaporisation of the base and its ignition in the possibly oxygen-enriched atmosphere.
See other AGITATION INCIDENTS

Iron(II) sulfate, Nitric acid, Sodium carboxymethylcellulose

1. Sansoni, B. *et al., Z. Anal. Chem.*, 1968, **243**, 209
2. Cela Torrijos, R. *et al., Chem. & Eng. News*, 1978, **56**(49), 51

A published analytical procedure [1] for decomposing the sodium salt with ferrous-sulfate/peroxide in nitric acid at pH 2 led to deflagration or explosion during the evaporation stage when applied to 10 g samples, but not with 5 g samples. Presence of sulfuric acid avoids the problem [2].

Iron(III) chloride, Hydrocarbons

Merrifield, 1988, 7—8

A 6000 m^3 aqueous refinery effluent containing sulfides and traces of hydrocarbons was to be treated to remove sulfides before discharge. Aqueous ferric chloride was added, followed by 1800 l of 50 wt% peroxide added over 40 min, and after a further 30 min an explosion occurred which blew off the lid of the treatment vessel. This was attributed to ignition of the explosive mixture of hydrocarbon vapours and oxygen (from iron-catalysed decomposition of peroxide) formed above the liquid surface.

See other GAS EVOLUTION INCIDENTS

Ketene

Swern, D., Chem. Rev., 1949, 45, 7

Interaction with excess ketene rapidly forms explosive diacetyl peroxide.

Ketones, Nitric acid

Bjorklund, G. H. *et al., Trans. R. Soc. Can., (Sect. III)*, 1950, **44**, 25

Unless the temperature and concentrations of reagents were carefully controlled, mixtures of hydrogen peroxide, nitric acid and acetone overheated and exploded violently. Under controlled conditions, the explosive dimeric or trimeric acetone peroxides were produced. 2-Butanone and 3-pentanone gave shock- and heat-sensitive oily peroxides. Cyclopentanone reacts vigorously, giving a solid which soon produces a series of explosions if left in contact with the undiluted reaction liquor. The isolated trimeric peroxide is very sensitive to shock, slight friction or rapid heating, and explodes very violently. Cyclohexanone and 3-methylcylohexanone gave oily, rather explosive peroxides.

See CYCLIC PEROXIDES, KETONE PEROXIDES

Lead, Trioxane

Bamberger, M. *et al., Z. Ges. Schiess-u. Sprengstoffw.*, 1927, **22**, 125—128

Mixtures of trioxane with 60% hydrogen peroxide solution are detonable by heat or shock, or spontaneously after contact with metallic lead. The latter may be owing to the heat of oxidation of lead.

See Metals, below

See also Oxygenated compounds, etc., below

Lithium tetrahydroaluminate

Osmon, R. V., *Chem. Eng. Progr. Symp. Ser.*, 1966, **62**(61), 92—102

This oxidiser—fuel combination showed promise in rocketry.

See other REDOX REACTIONS

Luggage

U.S. National Transportation Safety Board, Hazardous Materials Incident Brief, HZB-00/01, 2000

Polythene containers of approx. 35% peroxide, improperly carried as aircraft passenger baggage, broke, wetting adjacent areas and luggage. Several hours and a transfer later, two suitcases were found to be smouldering. That photographed is fabric (cotton or nylon?). Peroxide concentration by evaporation of water would be possible, as for Cotton waste, above.

Mercury(II) oxide, Nitric acid MRH Mercury(II) oxide 1.59/tr.

Mellor, 1940, Vol. 4, 781

Although red mercuric oxide usually vigorously decomposes hydrogen peroxide, the presence of traces of nitric acid inhibits decomposition and promotes formation of red mercury(II) peroxide. This explodes on impact or friction, even when wet, if the mercury oxide was finely divided.

Metals, or Metal oxides, or Metal salts

MRH Aluminium 12.76/35, iron 4.60/52, lithium 13.64/29, magnesium 12.68/41, silver, 1.59/tr., sodium 5.81/57; manganese dioxide, mercury(I) oxide, mercury(II) oxide, calcium permanganate, all 1.59/tr.

1. Mellor, 1939, Vol. 1, 936—944
2. Schumb, 1955, 480
3. Kit and Evered, 1960, 136
4. *Hydrogen Peroxide Data Manual*, Laporte Chemicals Ltd., Luton, 1960
5. Hardin, M. C. *et al., Chem. Abs.*, 1963, **59**, 2583h
6. Winnacker, 1970, Vol. 2, 552

The noble metals are all very active catalysts, particularly when finely divided or dispersed on high-area surfaces, for the decomposition of hydrogen peroxide, silver being used for this purpose in peroxide-powered rocket motors. Gold and the platinum group metals behave similarly [2,3,4]. Addition of platinum black to conc. peroxide solution may cause an explosion, and powdered magnesium and iron, promoted by traces of manganese dioxide, ignite on contact [1]. Potassium and sodium are oxidised violently by conc. peroxide solutions [1], and interaction of lithium and hydrogen peroxide is hypergolic and controllable under rocket motor conditions [5]. The effectiveness of metals for catalytic decomposition of peroxide solutions decreases in the order: osmium, palladium, platinum, iridium, gold, silver, manganese, cobalt, copper, lead [6]. Oxides of cobalt, iron (especially rust), lead (also the hydroxide), manganese, mercury and nickel are also very active and the parent metals and their alloys must be rigorously excluded from peroxide handling systems [1,4]. Soluble derivatives of many other metals, particularly under alkaline conditions, will also catalyse the exothermic decomposition, even at low concentrations [4]. Calcium permanganate has been used, either as a solid or in conc. solution, to ignite peroxide rocket motors [3]. Comprehensive data on all aspects of handling and use of conc. peroxide are available [4].

See Carbon, above

Methanol, *tert*-Amine, Platinum catalyst

Laughlin, R. G., *Chem. Eng. News*, 1978, **56**(19), 38

To solubilise a dialkylmethylamine during oxidation to the *N*-oxide with hydrogen peroxide, methanol was used as diluent in place of water. After oxide formation was complete, platinum black was added to decompose excess peroxide, and an explosion occurred. This was attributed to ignition of the methanol vapour—oxygen mixture by glowing catalyst particles.

See Oxygenated compounds, below

Methanol, Copper sulfate, Cyanide residues

Merrifield, 1988, 8

Aqueous cyanide effluent containing a little methanol in a 2 m^3 open tank was being treated to destroy cyanide by oxidation to cyanate with hydrogen peroxide in the presence of copper sulfate as catalyst. The tank was located in a booth with doors. Addition of copper sulfate (1 g/l) was followed by the peroxide solution (27 l of 35 wt%), and after the addition was complete an explosion blew off the doors of the booth. This was attributed to formation of a methanol vapour—oxygen mixture above the liquid surface, followed by spontaneous ignition. It seems remotely possible that unstable methyl hydroperoxide may have been involved in the ignition process.

See Waste treatment, below.

See other GAS EVOLUTION INCIDENTS

Methanol, Phosphoric acid

1. Anon., *J. Electrochem. Soc.*, 1965, **112**, 251C
2. King, C. V., *J. Electrochem. Soc.*, 1965, **112**, 1057; 1966, **113**, 519

In mixtures of the 3 components intended for use as chemical polishing or etching solutions [1], conc. peroxide must not be used [2].

See Oxygenated compounds, below

Methanol, sulfur trioxide

Wakakura, M. *et al., J. Loss Prev. Process Ind.*, 1999, **12**, 79

The product of a sulfation for surfactant manufacture was then bleached with hydrogen peroxide in aqueous methanol. Methanol was later recovered by distillation. At the end of distillation a violent explosion destroyed the top of the column, causing two fatalities. It is hypothesised that excess sulphur trioxide reacted with methanol to give methylsulfuric acid, which in turn methylated hydrogen peroxide to produce methyl hydroperoxide. This was concentrated in the late stages of methanol recovery, the final condensate possibly containing > 30% in iron equipment, leading to detonation. If the flow diagram published be believed, the substrate for sulfation was itself a methyl ester (between translation from the Japanese and origination by chemical engineer there may be doubt; esters are not usually surfactant), formation of methyl sulfuric acid, or the more reactive dimethyl sulfate, during sulfation then seems more probable than during the substantially aqueous bleach step.

See Methyl hydroperoxide

4-Methyl-2,4,6-triazatricyclo[5.2.2.$0^{2,6}$]undeca-8-ene-3,5-dione, Potassium hydroxide

1. Olsen, H. *et al., J. Amer. Chem. Soc.*, 1977, **99**, 1533
2. Engel, P. S. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 7107

Treatment of the dione dissolved in ethylene glycol—30% hydrogen peroxide with potassium hydroxide leads to a violently exothermic hydrolysis—*N*-oxidation reaction [1]. Simultaneous addition of peroxide and alkali solutions from separate funnels gives a controllable and higher yielding reaction [2].

Nitric acid, Soils

See Nitric acid: Hydrogen peroxide, Soils

Nitric acid, Thiourea

Bjorklund, G. H. *et al., Trans. R. Soc. Can., (Sect. III)*, 1950, **44**, 28
The solid peroxide produced by action of hydrogen peroxide and nitric acid on thiourea (and possibly a hydrogen peroxidate of thiourea dioxide) decomposed violently on drying in air, with evolution of sufur dioxide and free sulfur.
See CRYSTALLINE HYDROGEN PEROXIDATES

Nitriles

Wakakura, M. *et al., Netsu Sokutsei*, 1994, **21**(2), 68; *Chem. Abs.*, 1994, **121**, 57411f
A calorimetric study of the alkaline hydrogen peroxide conversion of organic nitriles to amides was undertaken. The reaction showed potential for runaway if carelessly scaled up.

Nitrogenous bases MRH values below references

1. Stone, F. S. *et al., J. Chem. Phys.*, 1952, **20**, 1339
2. Urbanski, 1967, Vol. 3, 306
3. *Haz. Chem. Data*, 1975, 296

MRH Ammonia, 5.86/25, aniline 6.44/17, dimethylhydrazine 6.69/19

Ammonia dissolved in 99.6% peroxide gave an unstable solution which exploded violently [1]. In the absence of catalysts, conc. peroxide does not react immediately with hydrazine hydrate. This induction period has caused a number of explosions and accidents owing to sudden reaction of accumulated materials [2]. 1,1-Dimethylhydrazine is hypergolic with high-test peroxide [3].
See other INDUCTION PERIOD INCIDENTS

Organic compounds MRH Acetic acid 5.10/31, ethanol 6.19/19

1. Hutton, E., *Chem. Brit.*, 1969, **5**, 287
2. *The Manufacture of Organic Chemicals using Hydrogen Peroxide*, AO 1.2, 36—37, Widnes, Interox Chemicals Ltd., 1979
3. Nolan, 1983, Case history 156
4. Merrifield, 1988, 8
5. Mackenzie, J., *Plant/Oper. Progr.*, 1991, **10**(3), 143
6. Klais, O., *Thermochim. Acta*, 1993, **225**(2), 213

Although under certain circumstances mixtures of hydrogen peroxide and organic compounds are capable of developing more explosive power than an equivalent wt of TNT, in many cases interaction can be effected safely and well under control by applying well-established procedures, to which several references are given [1]. A triangular diagram specifically for the system hydrogen peroxide—glycerol—water, but also generally applicable to other organic compounds, such as acetic acid, ethanol, aniline or quinoline, shows the range of detonable compositions, and gives guidance and examples on avoiding the hazardous regions in reaction systems [2]. A polyester was made from propylene glycol, adipic acid and aluminium stearate catalyst by distilling out the water of reaction at 230°C under nitrogen. A portion of hydrogen peroxide, added to bleach the product, failed to do this, so a second portion was added. The explosion which occurred later was attributed to accumulation of highly concentrated excess peroxide and traces of organic material (either volatile or entrained) in the reflux dividing head [3]. Only a few ppm of impurities are necessary to cause autodetonation of very concentrated hydrogen peroxide [4]. A survey of explosion hazards likely to be encountered from reagent use of hydrogen peroxide in organic chemistry is given [5]. Charging too concentrated peroxide to organic materials in surfactant manufacture caused a pressure increase which burst a pipe, starting a catalogue of mishap which destroyed the plant. Laboratory investigations showed that 10% peroxide by weight with ‘organic’ material could cause pressure surges in excess of the plant rating. The editor suspects this is base catalysed peroxide decomposition, the organic material being tertiary amines for amine oxide surfactants [6].

Organic materials, Sulfuric acid

Analytical Methods Committee, *Analyst*, 1976, **101**, 62—66

Advantages and potential hazards in the use of mixtures of 50% hydrogen peroxide solution and conc. sulfuric acid to destroy various types of organic materials prior to analysis are discussed in detail. The method is appreciably safer than those using perchloric and/or nitric acids, but the use of an adequate proportion of sulfuric acid with a minimum of peroxide is necessary to avoid the risk of explosive decomposition. The method is not suitable for use in pressure-digestion vessels (PTFE lined steel bombs), in which an explosion occurred at 80°C.

Organic solvents

Astbury, G. R., *Org. Proc. Res. & Dev.*, 2002, **6**(6), 893

Decomposition of hydrogen peroxide, even dilute, can generate an oxygen enriched headspace, explosive in presence of suitable organic vapours. The rising bubbles of oxygen can generate electrostatic charges sufficient for ignition, which is considered in detail. A technique for purging, without undue loss of solvent vapour, offering safe large scale hydrogen peroxide oxidation in flammable solvents is described

See also Waste treatment, below

Other reactants

Yoshida, 1980, 85—86

MRH values calculated for a wide range of 25 oxidisable or catalytically active materials are given.

Oxygenated compounds, Water

MRH Acetaldehyde 6.27/21, acetic acid 5.27/31, acetone 6.26/19, ethanol 6.19/19, formaldehyde 6.44/31, formic acid 3.30/58, methanol 5.98/34, 2-propanol 6.32/16, propionaldehyde 6.44/19

1. Monger, J. M. *et al., J. Chem. Eng. Data*, 1961, **6**(1), 23
2. Shanley, E. S., *Chem. Eng. News*, 1979, **57**(21), 43

The explosion limits have been determined for liquid systems containing hydrogen peroxide, water and acetaldehyde, acetic acid, acetone, ethanol, formaldehyde, formic acid, methanol, 2-propanol or propionaldehyde, under various types of initiation [1]. In general, explosive behaviour is noted where the ratio of hydrogen peroxide to water is > 1, and if the overall fuel—peroxide composition is stoicheiometric, the explosive power and sensitivity may be equivalent to those of glyceryl nitrate [2].

See Alcohols, above

2-Phenyl-1,1-dimethylethanol, Sulfuric acid

1. Winstein, S. *et al., J. Amer. Chem. Soc.*, 1967, **89**, 1661
2. Hedaya, E. *et al., Chem. Eng. News*, 1967, **45**(43), 73
3. Hiatt, R. R. *et al., J. Org. Chem.*, 1963, **28**, 1893

Directions given [1] for the preparation of 2-phenyl-1,1-dimethylethyl hydroperoxide by adding sulfuric acid to a mixture of the alcohol and 90% hydrogen peroxide are wrong [2] and will lead to explosion [3]. The acidified peroxide (30—50% solution is strong enough) is preferably added to the alcohol, with suitable cooling and precautions [2].

See Alcohols, above

See 2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide

See also Oxygenated compounds, etc., below

α-Phenylselenoketones

Reich, H. J. *et al., J. Amer. Chem. Soc.*, 1975, **97**, 5442

During conversion of the selenoketone to the nor-phenylselenoenones with hydrogen peroxide, care is necessary to control the strongly exothermic reaction. Under no circumstances should oxidation of amounts above 5 mmol be effected by adding the full amount of peroxide before oxidation has started.

Phosphorus MRH (Yellow) 7.78/27

Anon., *J. R. Inst. Chem.*, 1957, **81**, 473

If yellow or red phosphorus is incompletely immersed while undergoing oxidation in hydrogen peroxide solutions, heating at the air—solution interface can ignite the phosphorus and lead to a violent reaction. Such behaviour has been observed with peroxide solutions above 30% (110 vol) concentration.

Phosphorus(V) oxide MRH 1.59/tr.

Toennies, G., *J. Amer. Chem. Soc.*, 1937, **59**, 555

The extremely violent interaction of phosphorus(V) oxide and conc. hydrogen peroxide to give peroxomonophosphoric acid may be moderated by using acetonitrile as a diluent.

Poly(acetoxyacrylic acid lactone), Poly(2-hydroxyacrylic acid)

Anon., *Jahresber.*, 1978, 75

The complex peroxide formed by stirring the polymeric compounds with 30% peroxide solution and sodium hydroxide at 5°C for an hour, according to a patented procedure, was precipitated with methanol. After intensive vacuum drying at 1.3 mbar without heating, the product suddenly exploded.

See other POLYPEROXIDES

Polymer residues

Merrifield, 1988, 7

A jacketed polymerisation vessel had become coated internally by a build up of polymer residues, and the vessel was being cleaned by treatment with aqueous hydrogen peroxide. To 5000 l of water in the vessel was added 150 kg of 27 wt% peroxide solution, and the vessel was heated by application of 10 bar steam (180°C) to the jacket. After a few minutes an explosion occurred, attributed to spontaneous

ignition of a mixture of oxygen from the decomposing peroxide and monomer vapours produced by depolymerisation of the residue on the heated walls of the vessel.
See other GAS EVOLUTION INCIDENTS

2-Propanol
Merrifield, 1988, 7
A large volume (11.25 m^3) of mixed fatty acids was to be bleached by treatment with successive portions of 50 wt% hydrogen peroxide. 2-Propanol (450 l) was added to the acids (to improve the mutual solubility of the reactants). The first 20 l portion of peroxide (at 51°C) was added, followed after 1 min by a second portion. Shortly afterwards an explosion occurred, which was attributed to spontaneous ignition of a 2-propanol vapour—oxygen mixture formed above the surface of the liquid. Oxygen is almost invariably evolved from hydrogen peroxide reactions, and volatile flammable solvents are therefore incompatible components in peroxide systems.
See Alcohols, above
See other GAS EVOLUTION INCIDENTS

Sulfides
Editor's personal experience
Addition of 30% hydrogen peroxide to moderately strong sodium sulfide solutions produced superheating below the surface, followed by cavitational explosions sufficient to break laboratory glass beakers.

Sulfuric acid

1. Analytical Methods Committee, *Analyst*, 1967, **92**, 404
2. Dobbs, D. A. *et al., Chem. Eng. News*, 1990, **68**(17), 2
3. Erickson, T. V., *Chem. Eng. News*, 1990, **68**(33), 2
4. Anon., *Environment, Safety & Health Bull.*, 1993,**93**(2), 1
5. Stuart, R., Internet, 1991
6. Ames Lab. Yellow Alert 010216a, Internet, 2001

Evaporation of mixtures of excess 50% hydrogen peroxide solutions with sulfuric acid (10:1) leads to loud but non-shattering explosions of the peroxomonosulfuric acid formed [1]. A freshly-made mixture of equal volumes of sulfuric acid and 30% hydrogen peroxide, "Piranha Solution" used for cleaning glass frits, exploded violently on storage. Explosions have also been experienced when cleaning frits, when contamination with organic solvent was suspected. The mixture will, in any case, slowly evolve oxygen to pressurise sealed containers [2,3]. Piranha solution also burst its container after addition of nitric acid [4]. A similar mixture, also containing small quantities of lithium sulfate and selenious acid and intended as a digesting agent for soil samples, burst its container after twelve days undisturbed in a refrigerator. Such solutions are best not stored and, if stored, should not be sealed [5]. Another cleaning mix, richer in sulfuric than Piranha solution, caused ignition of a plastic fitting, described as nylon-like, which should properly have been a fluropolymer [6].
See Organic materials, Sulfuric acid, above

Tetrahydrothiophene
Koppel, H. C., *Chem. Eng. News*, 1974, **52**(39), 3

Preparative reactions involving oxidation of tetrahydrothiophene to the sulfoxide by slow addition of 37% peroxide solutions exploded violently on 3 occasions. No explanation is apparent, and similar reactions had been run uneventfully over a period of 10 years.

Tin(II) chloride MRH 1.21/85

Vickery, R. C. *et al., Chem. & Ind.*, 1949, 657

Interaction is strongly exothermic, even in solution. Addition of peroxide solutions of above 3 wt% strength causes a violent reaction.

Unsaturated compounds

Swern, 1971, Vol. 2, 432

In commercial-scale epoxidation of unsaturated organic compounds, 50—70% hydrogen peroxide is added during 2—8 h to the stirred mixture of unsaturated compound, aliphatic acid and acid catalyst at 50—80°C, the rate of addition being dependent on heat-transfer capacity of the reaction system. When 70% peroxide is being used, care must be taken to avoid the dangerous detonable region by ensuring that an exotherm has occurred before more than 25% of the hydrogen peroxide is added.

See Carboxylic acids

See also Organic compounds above

See also Oxygenated compounds, above

Vinyl acetate

Anon., *ABCM Quart. Safety Summ.*, 1948, **19**, 18

Vinyl acetate had been hydroxylated by treatment with excess hydrogen peroxide in presence of osmium tetraoxide catalyst. An explosion occurred while excess vinyl acetate and solvent were being removed by vacuum distillation. This was attributed to the presence of peracetic acid, formed by interaction of excess hydrogen peroxide with acetic acid produced by hydrolysis of the vinyl acetate.

Waste treatment

1. Anon., 1989, private communication.
2. Anon., *Eur. Chem. News*, 1992, **58**(1537), 34
3. Wehrum, W. L., *Process Safety Progr.*, 1993, **12**(4), 199
4. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203
5. Anon., *Loss Prev. Bull.*, 1991, (102), 17
6. Astbury, G. R., *Org. Proc. Res. & Dev.*, 2002, **6**(6), 893

In the interests of greater safety and environmental consciousness, a chemical factory which had previously used sodium hypochlorite to treat alkaline aqueous wastes containing methanethiol, other volatile sulfur compounds, methanol and possibly dimethyl ether, changed to 30% hydrogen peroxide. Shortly after, an explosion in the headspace shattered the vessel, killing a worker and breaking a pipe containing flammable solvent, leading to a fire which destroyed the factory. It appears that decomposition of peroxide in alkali had produced an oxygen enriched headspace, allowing the organic vapours therein to enter explosive limits despite a nitrogen purge. The actual source of ignition is unknown [1]. Another fatal explosion when treating effluent, NO containing off gas with peroxide, is reported, presumably by creation and ignition of an oxygen rich atmosphere containing organic vapours [2]. A

third waste treatment incident, possibly fuelled by acetone is reported [3]. An ignition mechanism, by means of electrostatic effects from bursting oxygen bubbles, is postulated [4], and implications considered in detail [6]. A related accident which killed 17 men was due to an explosion in a waste tank from a propylene oxide/styrene plant. This contained hydrocarbons over aqueous waste and evolved oxygen from decomposition of 'light peroxide' by-product decomposition. The headspace was nitrogen flushed. During maintenance the nitrogen flow was cut off for 34 hours, but oxygen readings remained low. Minutes after nitrogen purging was restarted the tank exploded. It is thought the oxygen meter may have been ill positioned [5].
See Methanol, Copper sulfate, Cyanide residues, above
See also Bases, above

Wood

1. *MCA Case History No. 1626*
2. *MCA Case History No. 1648*

Leakage from drums of 35% hydrogen peroxide onto a wooden pallet caused ignition of the latter when it was moved. Combustion, though limited in area, was fierce and took some time to extinguish [1]. Leakage of 50% peroxide onto supporting pallets under polythene sheeting led to spontaneous ignition and a fierce fire. Contact of 50% peroxide with wood does not usually lead to spontaneous ignition, but hot weather, dry wood (possibly catalytically contaminated) and the thermal insulation of the cover may have contributed to ignition [2].
See other PACKAGING INCIDENTS

Yeast

Bodenbaugh, J. H. *et al., J. Chem. Educ.*, 1988, **66**(5), 461—463
Hydrogen peroxide solution may be catalytically decomposed to give oxygen gas safely using dry yeast powder. (The active component is enzymatic.)
See other GAS EVOLUTION INCIDENTS, OXIDANTS, PEROXIDES

4472. Zinc hydroxide

[20427-58-1] **H_2O_2Zn**

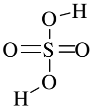
$$H-O^{-} \quad Zn^{2+} \quad O^{-}-H$$

Chlorinated rubber

See CHLORINATED RUBBER: METAL OXIDES OR HYDROXIDES

4473. Sulfuric acid

[7664-93-9] **H_2O_4S**



$$\begin{array}{c} O-H \\ | \\ O=S=O \\ | \\ H-O \end{array}$$

(*MCA SD-20*, 1963); *NSC 325*, 1982; *NSC 210*, 1967 (oleum); *FPA H31*, 1974; *HCS 1980*, 878, 879 (solutions), 702—704 (oleum); *RSC Lab. Hazards Safety Data Sheet No. 33*, 1985

The MCA Data Sheet covers safe handling procedures for all grades of sulfuric acid from fuming (oleum) through conc. to diluted acid. Coverage of the other series is as shown.

For an unusual incident involving static charge generation by sulfuric acid drops, *See* Hydrogen: Oxygen, Sulfuric acid

Acetaldehyde MRH 1.34/57
See Acetaldehyde: Sulfuric acid

Acetone, Nitric acid
See Nitric acid: Acetone, etc.

Acetonitrile, Sulfur trioxide
See Acetonitrile: Sulfuric acid

Acrylonitrile MRH 2.26/52
See Acrylonitrile: Acids

Alkyl nitrates MRH Methyl nitrate 6.53/99+
See ALKYL NITRATES: Lewis acids

2-Aminoethanol
Nolan, 1983, Case history 101
The two components are immiscible and must be stirred to effect conversion at 110°C to 2-aminoethyl hydrogen sulfate. A shift change led to the base being added to the acid without agitation. When the agitator was started later, reaction of the two cold and viscous layers of acid and base proceeded explosively.
See other AGITATION INCIDENTS

Ammonium iron(III) sulfate dodecahydrate
Clark, R. E. D., private comm., 1973
A few dense crystals heated with sulfuric acid exploded, owing to the exotherm in contact with water liberated as the crystals disintegrated.

Aniline, Glycerol, Nitrobenzene
See Quinoline

Benzyl alcohol MRH 1.13/52
Grignard, 1960, Vol. 5, 1005
A mixture of the alcohol with 58% sulfuric acid decomposes explosively at about 180°C.

Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.

tert-Butyl-*m*-xylene, Nitric acid
See Nitric acid: *tert*-Butyl-*m*-xylene, etc.

1-Chloro-2,3-epoxypropane

See 1-Chloro-2,3-epoxypropane: Sulfuric acid

4-Chloronitrobenzene, Sulfur trioxide

1. Grewer, T., *Chem. Ing. Tech.*, 1975, **47**, 233
2. Vervalin, C. H., *Hydrocarbon Process.*, 1976, **55**(9), 323
3. *See entry* SELF-ACCELERATING REACTIONS
4. Nolan, 1983, Case history 100

DTA shows that the reaction mixture from sulfonation of the nitro compound in 20% oleum, containing 35 wt% of 2-chloro-5-nitrobenzenesulfonic acid, exhibits 2 exothermic stages at 100 and 220°C, respectively, the latter being violently rapid. The adiabatic reaction mixture, initially at 89° attained 285°C with boiling after 17 h. At 180° the induction period was about 20 min [1]. Sulfonation of 4-chloronitrobenzene with 65% oleum at 46°C led to a runaway decomposition reaction in a 2000 l vessel. The original process using 20% oleum was less sensitive to heating rate and temperature. Knowledge that the reaction could be dangerous above 50°C had not been applied [2]. More thermoanalytical work has established safer operating conditions with a greater margin for remedial action [3]. In a further incident, the sulfonation (an established process) had been effected with 65% oleum at below 80°C, and the reaction mixture had been heated to, and held at 115°C, and then cooled to 80°C. Half of the batch was quenched in water with cooling to crystallise the product, but the remaining half in the reactor overheated and exploded. This was attributed to backflow of water from the quench tank into the reactor, and the exotherm from reaction of water with oleum led to exothermic decomposition of the sulfonic acid at around 160°C [4].

See THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

See other INDUCTION PERIOD INCIDENTS, SULFONATION INCIDENTS

Copper

Campbell, D. A., *School Sci. Rev.*, 1939, **20**(80), 631

The generation of sulfur dioxide by reduction of sulfuric acid with copper is considered too dangerous for a school experiment.

2-Cyano-2-propanol

1. *Occupancy Fire Record, FR 57-5*, 5, Boston, NFPA, 1957
2. Kirk-Othmer, 1967, Vol. 13, 333

Addition of sulfuric acid to the cyano-alcohol caused a vigorous reaction which pressure-ruptured the vessel [1]. This seems likely to have been caused by insufficient cooling to prevent dehydration of the alcohol to methacrylonitrile and lack of inhibitors to prevent exothermic polymerisation of the nitrile [2].

2-Cyano-4-nitrobenzenediazonium hydrogen sulfate

See 2-Cyano-4-nitrobenzenediazonium hydrogen sulfate: Sulfuric acid

Cyclopentadiene MRH 1.75/40

Wilson, P. J. *et al., Chem. Rev.*, 1944, **34**, 8

It reacts violently with charring, or explodes in contact with conc. sulfuric acid.

See Nitric acid: Hydrocarbons

Cyclopentanone oxime
See Cyclopentanone oxime: Sulfuric acid

1,3-Diazidobenzene
See 1,3-Diazidobenzene: Acids

Dichloromethane, Ethanol, Nitrate or nitrite
Dickie, R. J., private comm., 1981
The residues from a cortisol assay procedure (5 cc dichloromethane, 2.5 cc of a fluorescent reagent in 15:85 ethanol—sulfuric acid) were added to a 500 cc bottle and screw capped. After a 90 s delay, the bottle burst violently and brown fumes were seen. It was surmised that a nitrate or nitrite contaminant in the bottle had liberated oxides of nitrogen or nitric acid which had oxidised the organics exothermically.
See Nitric acid: Alcohols
See also Dinitrogen tetraoxide: Halocarbons

Diethylamine
Anon., *CISHC Chem. Safety Summ.*, 1984, **55**(218), 34—35
Diethylamine fumes from a reactor were usually absorbed in a glass scrubber through which sulfuric acid was circulated, but an unresolved fault in the level sensor caused the acid circulation pump to operate intermittently. While the pump was not running, amine fumes condensed in the dip pipe, forming a solid crust (of the sulfate) which allowed a quantity of condensed amine to accumulate out of contact with the acid. When the pump was restarted, the neutralisation exotherm was sufficient to shatter the scrubber and distort the mesh guard around it.
See other NEUTRALISATION INCIDENTS

Dimethoxydinitroanthraquinone
See mixo-Dimethoxydinitroanthraquinone: Sulfuric acid

4-Dimethylaminobenzaldehyde
MCA Case History No. 2101
During the preparation of a solution of the aldehyde in dilute sulfuric acid, the latter should be prepared before addition of the aldehyde. An attempt to prepare the solution by adding a slurry of the basic aldehyde in a little water to conc. sulfuric acid caused the stoppered flask to burst from the large exotherm generated by this procedure.

2,5-Dinitro-3-methylbenzoic acid, Sodium azide
See 2,5-Dinitro-3-methylbenzoic acid: Oleum, Sodium azide

1,5-Dinitronaphthalene, Sulfur
See 1,5-Dinitronaphthalene: Sulfur, etc.

Ethoxylated nonylphenol
Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 73
Breakage of glassware allowed 92% sulfuric acid into a heating bath containing hot Synperonic NX (nearly anhydrous ethoxylated nonylphenol, a liquid surfactant). Hydrolysis of the latter lowered the flashpoint and the bath ignited (possibly from formation of dioxane, flash point 12°C).

Hexalithium disilicide
See Hexalithium disilicide: Acids

Hydrofluoric acid
Bentzinger, von R. *et al., Praxis Naturwiss. Chem.*, 1987, 36, 37
A student was attempting to prepare anhydrous hydrogen fluoride by dehydrating aqueous 60% hydrogen fluoride solution with conc. sulfuric acid. Addition of 200 ml of sulfuric acid to 500 ml of hydrofluoric acid in a 1 l copper flask led to a rumbling noise, then a fountain from the flask neck of hot mixed acids which severely corroded the window glass and the floor tiles.
See Water, below
See other CORROSION INCIDENTS, GLASS INCIDENTS

Hydrogen peroxide MRH 1.59/99+
See Hydrogen peroxide: Sulfuric acid

Mercury nitride
See Mercury nitride: Alone, or Sulfuric acid

Metal acetylides or carbides MRH Calcium carbide 4.35/56
1. Mellor, 1946, Vol. 5, 849
2. *MCA SD-50*, 1963

Monocaesium and monorubidium acetylides ignite with conc. sulfuric acid [1]. Other carbides are hazardous in contact [2].

Metal chlorates MRH Sodium chlorate 1.30/99+
See METAL CHLORATES: Acids
See also METAL HALOGENATES: Metals, etc.

Metal perchlorates
See METAL PERCHLORATES: Sulfuric acid

4-Methylpyridine
Anon., *Loss. Prev. Bull.*, 1979, (029), 130—131
The base was added to 60 l of acid to convert it to the salt, but malfunction of the swivelling blade glass stirrer caused no agitation and the liquid base remained layered above the conc. acid. Switching off the stirrer caused it to become effective and the whole of the contents erupted from the 100 l flask as an acid mist.
See other AGITATION INCIDENTS, NEUTRALISATION INCIDENTS

Nitramide
See Nitric amide: Sulfuric acid

Nitric acid, Organic materials
See Nitric acid: Organic materials, Sulfuric acid

Nitric acid, Toluene
See Nitric acid: Hydrocarbons (reference 7)

Nitroaryl bases and derivatives MRH Nitroaniline 3.30/99+

1. Hodgson, J. F., *Chem. & Ind.*, 1968, 1399; private comm., 1973
2. Poshkus, A. C. *et al., J. Appl. Polym. Sci.*, 1970, **14**, 2049—2052

A series of 2- and 4-nitroaniline derivatives and analogues when heated with conc. sulfuric acid to above 200°C undergo, after an induction period, a vigorous reaction. This is accompanied by gas evolution which produces up to a 150-fold increase in volume of a solid foam, and is rapid enough to be potentially hazardous if confined. 2-Nitroaniline reacts almost explosively [1], and 4-nitroaniline, 4-nitroacetanilide, aminonitrobiphenyls, aminonitronaphthalenes and their various derivatives [2], as well as some nitro-N-heterocycles [1,2], also react vigorously. 4-Nitroanilinium sulfate and 4-nitroaniline-2-sulfonic acid and its salts also generate foams when heated without sulfuric acid. The mechanism is not clear, but involves generation of a polymeric matrix foamed by sulfur dioxide and water eliminated during the reaction [1].

See Diethyl sulfate: 2,7-Dinitro-9-phenylphenanthridine

See other GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS

Nitrobenzene

See Nitrobenzene: Sulfuric acid

3-Nitrobenzenesulfonic acid

See 3-Nitrobenzenesulfonic acid: Sulfuric acid

Nitro-explosives

Gamezo, V. N. *et al., J. Phys. IV*, 1995, **5**(C4), 395

The effect of sulphuric acid and oleum on the explosive properties of nitromethane, dinitrotoluene, trinitrobenzene and trinitrotoluene was studied. They are considerably sensitised.

See other nitro-derivatives, above and below

Nitromethane

See Nitromethane: Acids

N-Nitromethylamine

See *N*-Nitromethylamine: Sulfuric acid

4-Nitrotoluene

See 4-Nitrotoluene: Sulfuric acid

Other reactants

Yoshida, 1980, 393

MRH values calculated for 15 combinations with various materials are given.

Permanganates MRH Potassium permanganate 0.50/76

Interaction produces the powerful oxidant, permanganic acid.

See Permanganic acid: Organic materials
Potassium permanganate: Sulfuric acid

Phosphorus MRH (Red) 2.64/28

1. Mellor, 1940, Vol. 8, 786
2. Zschalich, A. *et al., Chem. Abs.*, 1993, 11532b
3. Urben, P. G., personal experience

White phosphorus ignites in contact with boiling sulfuric acid or its vapour [1]. An explosion hazard exists at industrial scale under milder conditions [2]. Even red phosphorus reacts vigorously with sulfuric acid in the presence of iodine or iodides, to produce hydrogen sulfide, from about 80°C [3].

Phosphorus(III) oxide
See Tetraphosphorus hexaoxide: Sulfuric acid

Poly(silylene)
See Poly(silylene): Oxidants

Potassium
See Potassium: Sulfuric acid

Potassium *tert*-butoxide
See Potassium *tert*-butoxide: Acids

3-Propynol
See 3-Propynol: Sulfuric acid

Silver permanganate
See Silver permanganate: Sulfuric acid

Silver peroxochromate

Sodium MRH 3.89/31
See Sodium: Acids

Sodium carbonate
See Sodium carbonate: Sulfuric acid

Sodium tetrahydroborate
See Sodium tetrahydroborate: Acids

Sodium thiocyanate
Meyer, 1977, 39
Violent exotherm on contact, carbonyl sulfide being evolved.

Steel
MARS Database, 1998, short report 021
Steel is normally considered a safe material for contact with (reasonably pure) sulphuric acid. However, this report is of a fatal explosion when working on a sulphuric acid tank with cutting torches, attributed to hydrogen in the headspace arising from corrosion of the metal ascribed to poor maintenance.

Sucrose

Meeks, E. G., *School Sci. Rev.*, 1979, **61**(215), 281—283

In the demonstration of the foaming carbonisation of sucrose by sulfuric acid, it has been found that about half of the gas produced is carbon monoxide and not carbon dioxide as previously supposed. (Other sugars and carbohydrates may be expected to behave similarly.)

See SUGARS

Tetramethylbenzenes

1. Birch, S. F. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 1364
2. Smith, L. I., *Org. Reactions*, 1942, Vol. 1, 382

Sulfonation of the mixed isomers of 1,2,3,5- and 1,2,4,5-tetramethylbenzenes was too violent [1], for shaking in a closed glass vessel as originally described [2].

See other SULFONATION INCIDENTS

1,2,4,5-Tetrazine

See 1,2,4,5-Tetrazine: Sulfuric acid

Thallium(I) azidodithiocarbonate

See Thallium(I) azidodithiocarbonate: Sulfuric acid

1,3,5-Trinitrosohexahydro-1,3,5-triazine

See 1,3,5-Trinitrosohexahydro-1,3,5-triazine: Sulfuric acid

Waste solvents

1. Langerman, N. *Chem. Health & Safety*, 2002, **9**(5), 39
2. Editor's comment

An account is given of exotherm and foaming consequent upon adding the acid to a waste solvent drum; materials known to be present were xylene and and butyl chloride [1]. Sulfuric acid would catalyse the Friedel Crafts reaction of these, evolving hydrogen chloride, though immiscibility means a delay might be expected and reaction seems to have been immediate [2].

Water

Mellor, 1947, Vol. 120, 405—408

Dilution of conc. sulfuric acid by water is vigorously exothermic and must be effected by adding acid to water to avoid local boiling. Mixtures of sulfuric acid and excess snow form powerful freezing mixtures. Fuming sulfuric acid (oleum, containing sulfur trioxide) reacts violently with water.

See 3-Nitrobenzenesulfonic acid: Sulfuric acid

Zinc iodide

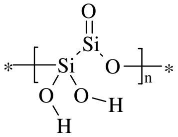
Pascal, 1962, Vol. 5, 168

Interaction with the conc. acid is violent.

See other INORGANIC ACIDS, OXIDANTS

4474. Poly(dihydroxydioxodisilane)

[ ] **$(H_2O_4Si_2)_n$**



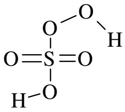
1. Sorbe, 1968, 127
2. Mellor, 1940, Vol. 6, 230

The dry compound explodes on impact or heating [1]. This polymeric product of hydrolysis of hexahalo- or hexaethoxy-disilane decomposes with more or less violence if heated in air (when it ignites) or in a test tube (when it explodes) [2].

See related NON-METAL OXIDES

4475. Peroxomonosulfuric acid

[7722-86-3] **H_2O_5S**



1. Edwards, J. O., *Chem. Eng. News*, 1955, **33**, 3336
2. Brauer, 1963, Vol. 1, 389

A small sample had been prepared from chlorosulfuric acid and 90% hydrogen peroxide; the required acid phase was separated and stored at 0°C overnight. After warming slightly, it exploded [1]. The handling of large amounts is dangerous owing to the possibility of local overheating (e.g., from contact with moisture) and explosive decomposition [2].

Acetone

1. *MCA Case History No. 662*
2. Bayer, A., *Ber.*, 1900, **33**, 858

Accidental addition of a little acetone to the residue from wet-ashing a polymer with mixed nitric—sulfuric acids and hydrogen peroxide caused a violent explosion [1]. The peroxoacid would be produced under these conditions, and is known to react with acetone to produce the explosive acetone peroxide [2], but direct oxidation of acetone may have been responsible.

Alcohols

1. Toennies, G., *J. Amer. Chem. Soc.*, 1937, **59**, 552
2. Merrifield, 1988, 6, 16

Contact of the acid with *sec*- or *tert*-alcohols, even with cooling, may lead to violent explosions [1]. The autodetonation region which exists for the hydrogen peroxide—sulfuric acid—2-propanol or —*tert*-butanol system is shown on a triangular diagram [2].

Aromatic compounds

Sidgwick, 1950, 939

Mixtures with aniline, benzene, phenol etc., explode.

Catalysts

Mellor, 1946, Vol. 5, 483—484

The 92% acid is decomposed explosively on contact with massive or finely divided platinum, manganese dioxide or silver. Neutralised solutions of the acid also froth violently on treatment with silver nitrate, lead dioxide or manganese dioxide.

Fibres

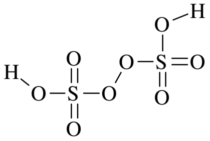
Ahrle, H., *Z. Angew. Chem.*, 1909, **23**, 1713

Wool and cellulose are rapidly carbonised by the 92% acid, while cotton ignites after a short delay.

See other INORGANIC ACIDS, OXIDANTS, PEROXOACIDS

4476. Peroxodisulfuric acid

[13445-49-3] **$H_2O_8S_2$**



Aromatic amines, Sulfuric acid

Nielsen, A. T. *et al., J. Org. Chem.*, 1980, **45**, 2341—2347

The acid, prepared from 90—98% hydrogen peroxide and oleum or 100% sulfuric acid, is one of the most powerful known oxidants and its use for oxidising aromatic amines to nitro compounds has been studied. Some mono- di- and tri-amines are destroyed exothermically with violent fume-off. Precautions for use are detailed.

Organic liquids

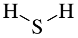
1. D'Ans, J. *et al., Ber.*, 1910, **43**, 1880; *Z. Anorg. Chem.*, 1911, **73**, 1911
2. Sidgwick, 1950, 938

A very powerful oxidant; uncontrolled contact with aniline, benzene, ethanol, ether, nitrobenzene or phenol may cause explosion [1]. Alkanes are slowly carbonised [2].

See other OXIDANTS, PEROXOACIDS

†4477. Hydrogen sulfide

[7783-06-4] **H_2S**



(*MCA SD-36*, 1968); *NSC 284*, 1977; *FPA H78*, 1979; *HCS 1980*, 553 (cylinder); *RSC Lab. Hazards Safety Data Sheet No. 35*, 1985

1,2-Bis(2-azidoethoxy)ethane, Ethanol
See 1,2-Bis(2-azidoethoxy)ethane: Ethanol, etc.

4-Bromobenzenediazonium chloride
See DIAZONIUM SULFIDES AND DERIVATIVES

Copper, Oxygen
Merz, V. *et al., Ber.*, 1880, **13**, 722
Addition of powdered copper to a 1:2 mixture of hydrogen sulfide and oxygen causes the metal to become incandescent and ignite the explosive mixture.
See Metals, below

Metal oxides MRH Copper oxide 1.05/70, chromium trioxide 2.05/88, lead dioxide 0.54/78, manganese dioxide 0.84/94, sodium peroxide 3.01/70
Mellor, 1947, Vol. 10. 129, 141
Hydrogen sulfide is rapidly oxidised, and may ignite in contact with a range of metal oxides, including barium peroxide, chromium trioxide, copper oxide, lead dioxide, manganese dioxide, nickel oxide, silver(I) oxide, silver(II) oxide, sodium peroxide, and thallium(III) oxide. In the presence of air, contact with mixtures of calcium oxide or barium oxide with mercury oxide or nickel oxide may cause vivid incandescence or explosion.
See Rust, below

Metals
Mellor, 1947, Vol. 10, 140; 1943, Vol. 11, 731
A mixture with air passed over copper powder may attain red heat. Finely divided tungsten glows red hot in a stream of hydrogen sulfide.
See Copper, Oxygen, above
See also Sodium: Sulfides

Nitrogen trichloride
See Nitrogen trichloride: Initiators

Other reactants
Yoshida, 1980, 390
MRH values calculated for 11 combinations with oxidants are given.

Oxidants MRH values show % of oxidant
See Metal oxides, above; Oxygen, and Rust, both below

Bromine pentafluoride: Hydrogen-containing materials	MRH 3.01/70
Chlorine trifluoride: Hydrogen-containing materials	MRH 2.05/88
Chromium trioxide: Hydrogen sulfide	
Copper chromate oxide: Hydrogen sulfide	
Dibismuth dichromium nonaoxide: Hydrogen sulfide	
Dichlorine oxide: Oxidisable materials	MRH 3.22/91
Fluorine: Hydrogen sulfide	MRH 9.29/72
Heptasilver nitrate octaoxide: Alone, or Sulfides	
Lead(II) hypochlorite: Hydrogen sulfide	
Lead(IV) oxide: Hydrogen sulfide	MRH 0.54/78

Mercury(I) bromate: Hydrogen sulfide
Nitric acid: Non-metal hydrides MRH 4.43/74
Oxygen difluoride: Combustible gases
Perchloryl fluoride: Hydrocarbons, etc.
Silver bromate: Sulfur compounds
Sodium peroxide: Hydrogen sulfide MRH 3.01/70

Oxygen

Gray, P. *et al., J. Chem. Soc., Faraday Trans. 1*, 1974, **70** 2338—2350

During an investigation of the spontaneously explosive oxidation of near-stoicheiometric gas mixtures in the range 280—360°C, extensive self-heating was observed before ignition occurred. The second and third ignition limits were also investigated.

See Oxidants, above

Rust

Mee. A. J., *School Sci. Rev.*, 1940, **22**(85), 95

Hydrogen sulfide may ignite if passed through rusty iron pipes.

See Metal oxides, above

Silver fulminate

See Silver fulminate: Hydrogen sulfide

Soda-lime

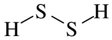
1. Mellor, 1947, Vol. 10, 140
2. Bretherick, L., *Chem. & Ind.*, 1971, 1042

Interaction is exothermic, and if air is present, incandescence may occur with freshly prepared granular material. Admixture with oxygen causes a violent explosion [1]. Soda-lime, used to absorb hydrogen sulfide, will subsequently react with atmospheric oxygen and especially carbon dioxide (from the solid coolant) with a sufficient exotherm in contact with moist paper wipes (in a laboratory waste bin) to cause ignition [2]. Spent material should be saturated with water before separate disposal. Mixture analogous to soda-lime, such as barium hydroxide with potassium or sodium hydroxides, also behave similarly [1].

See other NON-METAL HYDRIDES, NON-METAL SULFIDES, SELF-HEATING AND IGNITION INCIDENTS

†4478. Hydrogen disulfide

[13465-07-1] H_2S_2



Alkalies

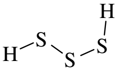
Bloch, I. *et al., Ber.*, 1908, **41**, 1977

Rather more flammable than hydrogen trisulfide, it is decomposed violently by alkalies.

See other NON-METAL HYDRIDES, NON-METAL SULFIDES

4479. Hydrogen trisulfide

[13845-23-3] **H_2S_3**



Benzenediazonium chloride

King, W. B. *et al., J. Amer. Chem. Soc.*, 1932, **54**, 3073

Addition of the dry diazonium salt to the crude liquid sulfide causes explosively violent interaction. Slow addition of the sulfide to the cooled salt, or dilution with a solvent, moderates the reaction.

See other DIAZONIUM SULFIDES AND DERIVATIVES

Metal oxides

Mellor, 1947, Vol. 10, 159

Contact with copper oxide, lead(II) oxide, lead(IV) oxide, mercury(II) oxide, tin(IV) oxide or iron(II,III) oxide causes violent decomposition and ignition. Dry powdered silver oxide causes an explosion.

Nitrogen trichloride

See Nitrogen trichloride: Initiators

Pentanol

Mellor, 1947, Vol. 10, 158

Interaction is explosively violent.

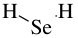
Potassium permanganate

See Potassium permanganate: Hydrogen trisulfide

See other NON-METAL HYDRIDES, NON-METAL SULFIDES

†4480. Hydrogen selenide

[7783-07-5] **H_2Se**



It is moderately endothermic (ΔH_f° (g) +85.8 kJ/mol, 1.06 kJ/g).

Oxidants

See Hydrogen peroxide: Hydrogen selenide

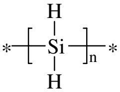
Nitric acid: Non-metal hydrides

See other ENDOTHERMIC COMPOUNDS, NON-METAL HYDRIDES

See related NON-METAL SULFIDES

4481. Poly(silylene)

[32078-95-8] **$(H_2Si)_n$**

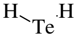


Brauer, 1963, Vol. 1, 682
The dry solid ignites in air.

Oxidants
Bailar, 1973, Vol. 1, 1352
It ignites in contact with conc. nitric acid and explodes with sulfuric acid.
See related SILANES

†4482. Hydrogen telluride

[7783-09-7] **H_2Te**

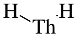


It is moderately endothermic (ΔH_f° (g) +154.4 kJ/mol, 1.19 kJ/g).

Nitric acid
See Nitric acid: Non-metal hydrides
See other ENDOTHERMIC COMPOUNDS, METAL HYDRIDES
See related NON-METAL HYDRIDES

4483. Thorium dihydride

[16689-88-6] **H_2Th**

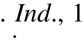


1. Hartmann, I. *et al., Rept. Invest. No. 4835*, Washington, US Bur. Mines, 1951
2. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74

Extremely pyrophoric when powdered [1], and is also a significant dust exploion hazard [2].
See other METAL HYDRIDES, PYROPHORIC MATERIALS

4484. Titanium dihydride

[7704-98-5] **H_2Ti**

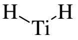


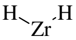
1. Alekseev, A. G. *et al., Chem. Abs.*, 1974, **81**, 123688
2. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74

Pyrophoricity and detonation behaviour of titanium hydride powders of various particle sizes were studied in comparison with those of titanium metal powders [1]. Maximum dust explosion pressures of 8.2 bar, with a maximum rate of rise of 816 bar/s have been recorded [2].
See Zirconium (reference 6)
See other METAL HYDRIDES, PYROPHORIC MATERIALS

4485. Titanium—zirconium hydride

[57425-12-4] **$H_2Ti.H_2Zr$**

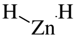




See Zirconium (reference 6)
See other METAL HYDRIDES

4486. Zinc hydride

[14018-82-7] **H_2Zn**

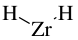


Barbaras, G. D. *et al., J. Amer. Chem. Soc.*, 1951, **73**, 4587
Fresh samples reacted slowly with air, but aged and partly decomposed samples (containing finely divided zinc) may ignite in air.

Acids, Water
Ashby, E. C. *et al., Inorg. Synth.*, 1977, **17**, 9
Hydrolysis with water occurs slowly, but is violent with aqueous acids.
See other METAL HYDRIDES

4487. 'Zirconium hydride'

[7704-99-6] **H_2Zr**

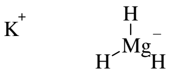


1. Mellor, 1941, Vol.7, 114
2. Sidgwick, 1950, 633
3. Baumgart, H., *Chem. Abs.*, 1985, **103**, 73412
4. Kuroda, E. *et al., Chem. Abs.*, 1997, **127**, 150727x

The product of sorbing hydrogen on to hot zirconium powder burns with incandescence when heated in air [1,2]. Ignition and combustion properties of pyrophoric zirconium and zirconium hydride powder (<10 μ), and safety measures are discussed [3]. Ignition energies for zirconium hydrides, ZrH_x; x = 0-2, in air have been studied in Japan [4].
See Zirconium (reference 6)
See other METAL HYDRIDES

4488. Potassium trihydomagnesate

[27071-36-9] **H_3KMg**

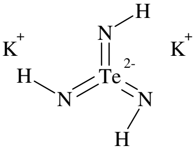


Ashby, E. C. *et al., Inorg. Chem.*, 1970, **92**, 2182

The solid reacted violently on exposure to atmospheric air.
See other COMPLEX HYDRIDES

4489. Dipotassium triimidotellurite

[ ] **$H_3K_2N_3Te$**

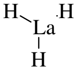


1. Schmitz-Du Mont, O. *et al., Angewand. Chem. (Int.)*, 1967, **6**, 1071
2. Chivers, T. *et al., Angewand. Chem. (Int.)*, 1995, **34**(22), 2549

Colourless crystals, exploding on contact with water unless benzene damp. Ammonolysis converts it to the still more explosive tritellurium tetranitride [1]. Highly explosive [2].
See also N—S COMPOUNDS

4490. Lanthanum hydride

[13864-01-2] **H_3La**

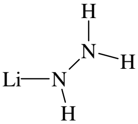


1. Mackay, 1966, 66

It ignites in air.
See other METAL HYDRIDES

4491. Lithium hydrazide

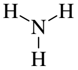
[37067-42-8] **H_3LiN_2**



Hydrazine and its Derivatives, Schmidt, F. W., New York, Wiley, 1984, 75
Merely smouldering on contact with air, it is claimed to be a safe metal hydrazide.
See other METAL HYDRAZIDES

†4492. Ammonia

[7664-41-7] **H_3N**



(*MCA SD-8*, 1960); *NSC 251*, 1979; *FPA H13*, 1973; *HCS 1980*, 139 (cylinder), 140 (25% solution); *RSC Lab. Hazards Safety Data Sheet No. 37*, 1985

1. *MCA SD-8*, 1960
2. Anon., *ABCM Quart. Safety Summ.*, 1950, **45**, 14
3. Anon., *ABCM Quart. Safety Summ.*, 1974, **45**, 14
4. Unpublished observations, 1968—1974
5. Henderson, D., *Ammonia Plant Safety*, 1975, **17**, 132—134
6. Krivulin, V. N. *et al., Chem. Abs.*, 1976, **84**, 124132
7. Harris, G. F. P. *et al., Proc. 6th Symp. Chem. Proc. Haz. Ref. Plant Des.*, 29—38, Symp. Ser. 49, Rugby, IChE, 1977
8. McRae, M. H., *Plant/Oper. Progr.*, 1987, **6**(1), 17—19
9. Klem, T. J., *Ammonia Plant Saf.*, 1987, (26), 145—149
10. Andersson, B. O., *Hazards XI*, 15, Symp. Ser. **124**, Rugby(UK), IChE, 1991.
11. Andersson, B. O., *Ammonia Plant Safety*, 1991, **31**, 5
12. Carlsson, T. O. *et al., Sci. Tech Froid*, 1996, (3), 277
13. Vasil'ev, A. A., et al., Arch. Combust., 2000, 20(3/4), 49
14. Vandebroek, L. et al., J. Haz. Mat., 2002, 93(1), 123

Although there is a high lower explosive limit in air and ignition is not easy, there is a long history of violent gas—air explosions in refrigeration practice, in which ammonia previously was used widely [1]. Mixtures of ammonia and air lying within the explosive limits can occur above aqueous solutions of certain strengths. Welding operations on a vessel containing aqueous ammonia caused a violent explosion [2]. Several incidents involving sudden 'boiling' of conc. ammonia solution (*d*, 0.880, 35 wt%) have occured when screw-capped winchesters are opened [3,4]. These are attributable to supersaturation of the solution with gas, caused by increase in temperature subsequent to preparation and bottling. The effect is particularly marked with winchesters filled in winter and opened in summer. Usually boiling-off begins immediately the cap is loosened, and if this is done carefully using gloves and eye-protection in a fume cupboard or under local extract ventilation, no great problems arise [4]. However a bottle which had been gently and successfully opened in this way without boiling-off subsequently erupted violently when the surface of the liquid was disturbed by a pipette [3]. This hazard may be avoided by using the slightly less concentrated solution (*d*, 0.990, 25 wt%) where this is technically acceptable.

There is an account of an incident involving combustion/explosion in the free space of a weak ammonia liquor tank where detailed examination revealed no evidence for an ignition source [5]. The existence of ammonia—air mixtures able to burn only in sufficiently large enclosed volumes was established [6]. Previous data on flammability has been summarised and extended by determination of flammability characteristics of ammonia admixed with dry air and oxygen-deficient air at temperatures from ambient up to 400°C. Similar work with added water vapour at 80°C shows that aqueous solutions of below 5% ammonia content do not produce flammable vapours at any temperature, and that above 49°C no flammable vapours are produced by ammonia solution of any concentration. Some data on ignition energy and explosibility are also given [7]. Two US incidents serve as a reminder of the considerable explosive potential of ammonia—air mixtures in confined volumes. An ice-cream factory with ammonia refrigeration plant which had been installed over 50 years previously had not been upgraded to meet modern engineering practice and electrical fire codes. There were no check valves or oil separators in the compressor discharge lines, and the plant was lit by unprotected tungsten filament lamps. During the night an ammmonia leak developed in the basement, and a few minutes later there was a violent explosion which largely destroyed the building. The major devastation prevented identification of the cause of the leak or of the ignition source, and it was postulated that oil mist may have been involved in initiating the explosion [8]. During an attempt to isolate a leak in the anhydrous ammonia refrigeration system in a cold store warehouse, an electric fork lift truck was to be used to replace a faulty valve. The truck crashed into an internal wall and the large explosion which followed no doubt involved spark ignition of the flammable atmosphere [9]. Both incidents revealed a widespread belief that ammonia is non-flammable, possibly arising from the US classification of anhydrous ammonia in cylinders as ‘a non-flammable gas’. In Europe, it is realistically classified as flammable, as also are highly concentrated aqueous solutions. With returning interest in it as a domestic refrigerant, studies of ignition energies and flame propagation in mixtures with air have been performed [12]. Explosion hazards with oxygen and nitrous oxide have also been reviewed [13]. Autoignition temperatures are considerably lowered by methane or hydrogen impurity [14].

A report is given of explosion of a tank containing 7000 t of liquid ammonia, in Lithuania, consequent upon thermal disequilibrium and ‘bumping’ of the liquid [10,11]. The liberated ammonia caught fire in the open air, the first time this is thought to have been observed.

See Nitric acid: Manufacture hazard

Air, Hydrocarbons

Kalkert, N. *et al., Chem. Ing. Tech.*, 1979, **51**, 895

Explosion limits have been estimated for mixtures containing C_1—C_3 hydrocarbons.

Air, Rust

Verduijn, W. D., *Process Safety Progress*, 1996, **15**(2), 89; Verduijn, W. D. *Ammonia Plant Safety*, 1996,

An account is given of a sequence of mishaps starting with a burst pipe in a nitric acid plant, apparently due to pre-ignition by rust catalysis of an ammonia/air mixture at 220°C and 11 bar.

Boron halides

Sidgwick, 1950, 380

The boron halides react violently with ammonia.

Calcium

See Calcium: Ammonia

Chlorine azide

See Chlorine azide: Alone, or Ammonia

1-Chloro-2,4-dinitrobenzene

See 1-Chloro-2,4-dinitrobenzene: Ammonia

Chloroformamidinium nitrate

See Chloroformamidinium nitrate: Alone, or Amines, etc.

1,2-Dichloroethane

491M, 1975, 36

Liquid ammonia and the solvent may explode when mixed. (It is possible this was a liquefied gas (physical) explosion, rather than an exothermic chemical reaction.)

See LIQUEFIED GASES

Ethanol, Silver nitrate

See Silver nitrate: Ammonia, Ethanol

Ethylene oxide

See Ethylene oxide: Ammonia

Germanium derivatives

Paschenko, I. S. *et al., Chem. Abs.*, 1976, **84**, 8568

'Causes of the Explosiveness of Gas—Liquid Mixtures during Neutralisation of Germanium-containing Solutions by Ammonia' (title only translated).

See Germanium imide

Gold(III) chloride

See Gold(III) chloride: Ammonia, etc.

Halogens, or Interhalogens

Ammonia either reacts violently, or produces explosive products, with all 4 halogens and some of the interhalogens.

See Bromine: Ammonia
Bromine pentafluoride: Hydrogen-containing materials
Chlorine trifluoride: Hydrogen-containing materials
Chlorine: Nitrogen compounds
Fluorine: Hydrides
Iodine: Ammonia

Heavy metals

Ammonia is capable of reacting with some heavy metal compounds (silver, gold, mercury) to produce materials, some of uncertain constitution, which may explode violently when dry.

See Gold(III) chloride: Ammonia
Mercury: Ammonia
Potassium triamidothallate ammoniate
Silver azide: Ammonia
Silver chloride: Ammonia
Silver nitrate: Ammonia
Silver(I) oxide: Ammonia

See N-METAL DERIVATIVES

Iodine, Potassium

Staley, S. W. *et al., Tetrahedron*, 1975, **31**, 1133

During the reductive cleavage of cyclopolyenes with potassium in liquid ammonia, the intermediate anionic species are quenched with iodine—pentane mixtures. The possibility of formation of explosive nitrogen triiodide and the need for precautions are stressed.

Magnesium perchlorate
See Magnesium perchlorate: Ammonia

Mercury
1. Marsch, H. D., *Ammonia Plant Safety*, 1991, **31**, 8
2. Wilhelm, S. M., *Ammonia Plant Safety*, 1991, **31**, 20

An explosion rupturing an ammonia separator (still) in an ammonia production unit, probably because mercury vapour from geological sources entered with hydrogen syngas originating from natural gas and reacted to give explosive nitride deposits. The separator remains crackled when scraped [1]. For a more academic study of the effects of mercury on ammonia plants, including embrittlement and corrosion, as well as explosive deposits [2].
See Mercury: Ammonia
See other CORROSION INCIDENTS

Nitrogen trichloride
See Nitrogen trichloride: Initiators

2-, or 4-Chloronitrobenzene
See 2-Chloronirobenzene: Ammonia or 4-Chloronitrobenzene: Ammonia

Other reactants
Yoshida, 1980, 36
MRH values calculated for 16 combinations, largely with oxidants, are given.

Oxidants — MRH values show % of oxidant
Maslonka, F., *Chem. Abs.*, 1978, **88**, 193935
The flammability and explosion susceptibility of ammonia is reviewed, with thermochemical data, explosion limits for various oxidants, and explosion parameters, both for the gas and its conc. aqueous solutions.
See Ammonium peroxodisulfate: Ammonia, etc.
Chromium trioxide: Ammonia
Chromyl chloride: Ammonia
Dichlorine oxide: Oxidisable materials
Dinitrogen tetraoxide: Ammonia
Hydrogen peroxide: Nitrogenous bases — MRH 5.86/75
Nitric acid: Ammonia — MRH 5.10/69
Nitrogen oxide: Ammonia
Nitryl chloride: Inorganic materials
Oxygen (Liquid): Ammonia, etc.
Potassium chlorate: Ammonia — MRH 4.31/78
‘Trioxygen difluoride’: Various materials

Oxygen, Platinum
See Oxygen (Gas): Ammonia, Platinum

Ozone
See Ozone: Ammoniacal vapours

Pentaborane(9)
See Pentaborane(9): Ammonia

Silver compounds
See Silver azide: Ammonia
Silver chloride: Ammonia
Silver nitrate: Ammonia
Silver(I) oxide: Ammonia, etc.

Stibine
See Stibine: Ammonia

Sulfinyl chloride
See Sulfinyl chloride: Ammonia

Tellurium halides
See Tellurium tetrabromide: Ammonia
Tellurium tetrachloride: Ammonia

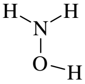
Tetramethylammonium amide
See Tetramethylammonium amide: Ammonia

Thiocarbonyl azide thiocyanate
See Thiocarbonyl azide thiocyanate: Ammonia, etc.

Thiotrithiazyl chloride
See Thiotrithiazyl chloride: Ammonia
See other INORGANIC BASES, NON-METAL HYDRIDES

4493. Hydroxylamine

[7803-49-8] **H_3NO**



HCS 1980, 557

1. Ashford, J. S., private comm., 1967
2. Brauer, 1963, Vol. 1, 502
3. Vervalin, C. H., *Hydrocarbon Proc. Petr. Ref.*, 1963, **42**(2), 174
4. Rüst, 1948, 302
5. Bailar, 1973, Vol. 2, 272
6. Anon., *Chemical Engineer*, 1999, 673, 3
7. Schiavo, C., *The Morning Call*, June 15 & Sept 8 (inter alia), 2000

8. Reisch, M., *Chem. Eng. News*, 2002, **80**(22), 6
9. Cisneros, O. L. *et al., J. Haz. Mat.*, 2001, **82**(1), 13
10. Tamura, M. *Chem. Abs.*, 2002, **136**, 267248u
11. Long, L. A., *Proceedings of the 37th Annual Loss Prevention Symposium*, 437, Amer. Inst. Chem. Eng., 2002
12. Iwata, Y. *et al., J. Haz. Mat.*, 2003, **104**(1-3), 39
13. Wei, C. *et al., Thermochim. Acta*, 2004, **421**(1-2), 1
14. Iwata, y. *et al., Process Safety Progress*, 2002, **21**(2), 136

The base was being prepared by distilling a mixture of hydroxylamine hydrochloride and sodium hydroxide in methanol under reduced pressure, and a violent explosion occurred towards the end of distillation [1], probably owing to an increase in pressure above 53 mbar. It explodes when heated under atmospheric pressure [2]. Traces of hydroxylamine remaining after reaction with acetonitrile to form acetamide oxime caused an explosion during evaporation of solvent. Traces can be removed by treatment with diacetyl monoxime and ammoniacal nickel sulfate, forming nickel dimethylglyoxime [3]. An account of an extremely violent explosion towards the end of vacuum distillation had been published previously [4]. Anhydrous hydroxylamine is usually stored at 10°C to prevent internal oxidation —reduction reactions which occur at ambient temperature [5]. An explosion throwing debris three kilometres, with five fatalities, appears to have been during industrial distillation of hydroxylamine in a not fully commissioned chemical plant [6]. Subsequent local newspaper reports make it apparent that it was a 50% aqueous solution that was to be distilled, though it may have become overconcentrated. A photograph of the consequences accompanies an article on runaways [8]. Fuller reports appeared later [11]. Extensive calorimetric studies on the stability of the 50% aqueous mix show it fairly stable in glass to above 100°C but destabilised by the usual metals of chemical plant construction [9,12]. Stabilisers are also studied [9]. Destabilisation by acid and base have also been shown [13]. Another plant, in Japan, preparing the same, or even more concentrated, solution for semi-conductor uses, also blew up two years later, with more fatalities [10]. The exact scale of operation remains unclear in both cases but must have been into the hundred kilogram range. The theoretical decomposition energy of hydroxylamine is about 5 kJ/g. This implies that a 50% solution might prove detonable in bulk, if tested [7]. Extensive testing of decomposition over a range of concentrations showed detonation above 80%, and much reduced stability in stainless steel DTA cells relative to gilt ones [14].

See other REDOX REACTIONS

Aldehyde (unspecified), Pyridine

MCA Guide, 1972, 300

During the preparation of an unspecified aldoxime, the ethanolic reaction mixture was extracted with ether and the extract was concentrated by vacuum distillation from a bath at 70—80°C. Towards the end of distillation violent decomposition occurred (probably of traces of unreacted hydroxylamine in the extract).

See above

Barium oxide MRH 3.86/tr.

See Oxidants, below

Carbonyl compound (unspecified), Pyridine

Anon., *Chem. Processing* (Chicago), 1963, **26**(24), 30

During preparation of an unspecified oxime, the carbonyl compound, pyridine, hydroxylamine hydrochloride and sodium acetate were heated in a stainless steel autoclave. At 90°C a sudden reaction caused a pressure surge to 340 bar, when the bursting disk failed. The reaction had been run previously and uneventfully on one-tenth scale in a glass lined autoclave.

See Metals, below

Copper(II) sulfate

Mellor, 1940, Vol. 8, 290

Hydroxylamine ignites with the anhydrous salt (possibly owing to heat of coordination).

Hydrogenation catalyst, Acid, Fuel

Riesthuis, P. *et al., J. Loss Prev. Process Ind.*, 1997, **10**(10), 67

In the presence of precious metal hydrogenation catalyst, hydroxylamine salts may disproportionate and form dinitrogen monoxide. Such a mixture is present in a process whereby the hydroxyamine is formed by hydrogenation of nitrate. An explosion in the degassing line, after a period of abnormal operation, was attributed to nitrous oxide build-up. Fuel, in the form of hydrogen and methane diluent, was already present.

See Dinitrogen oxide

Metals MRH Calcium, sodium, zinc all 3.85/tr.

1. Mellor, 1940, Vol. 8, 292
2. Sorbe, 1968, 158

Sodium ignites in contact with hydroxylamine alone, but reacts smoothly in ether solution to give *N*-sodium hydroxylamide which may be pyrophoric in air. Calcium reacts to give the bis(hydroxylamide) which explodes at 180°C. Finely divided zinc either ignites or explodes when warmed in contact with hydroxylamine [1]. Zinc and hydroxylamine form the bis(hydroxylamide) solvated with hydroxylamine (3 mol), an explosive compound [2].

See also OXIMES

Other reactants

Yoshida, 1980, 286

MRH values calculated for 16 combinations with various materials are given.

Oxidants MRH values below references show % of oxidant

1. Brauer, 1963, Vol. 1, 502
2. Mellor, 1930, Vol. 3, 670; 1940, Vol. 8, 287—294

MRH Barium peroxide 3.85/tr., calcium hypochlorite 3.77/52, lead dioxide 1.92/64, potassium dichromate 3.85/tr., potassium permanganate 2.80/49, sodium hypochlorite 3.97/53

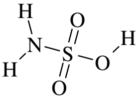
Hydroxylamine is a powerful reducant, particularly when anhydrous, and if exposed to air on a fibrous extended surface (filter paper) it rapidly heats by aerobic oxidation. It explodes in contact with air above 70°C [1]. Barium peroxide will ignite aqueous hydroxylamine, while the solid ignites in dry contact with barium oxide,

barium peroxide, lead dioxide and potassium permanganate, but with chlorates, bromates and perchlorates only when moistened with sulfuric acid. Contact of the anhydrous base with potassium dichromate or sodium dichromate is violently explosive, but less so with ammonium dichromate or chromium trioxide. Ignition occurs in gaseous chlorine, and vigorous oxidation occurs with hypochlorites [2].
See other REDOX REACTIONS

Phosphorus chlorides MRH Phosphorus(III) & (V) chlorides both 3.85/tr.
Mellor, 1940, Vol. 8, 290
The base ignites in contact with phosphorus trichloride and phosphorus pentachloride.
See also HYDROXYLAMINIUM SALTS
See other N—O COMPOUNDS, REDUCANTS

4494. Amidosulfuric acid (Sulfamic acid)

[5329-14-6] **H_3NO_3S**



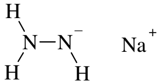
HCS 1980, 869

Chlorine
See Chlorine: Nitrogen compounds (reference 7)

Metal nitrates or nitrites
See METAL AMIDOSULFATES
See other INORGANIC ACIDS, N—S COMPOUNDS

4495. Sodium hydrazide

[13598-47-5] **H_3N_2Na**

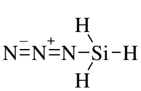


Air, or Ethanol, or Water
1. Mellor, 1940, Vol. 8, 317
2. Kauffmann, T., *Angew. Chem. (Intern. Ed.)*, 1964, **3**, 342

Contact with traces of air, ethanol or water causes a violent explosion [1], as does heating to 100°C [2].
See other METAL HYDRAZIDES

4496. Azidosilane

[13847-60-4] **H_3N_3Si**



Preparative hazard

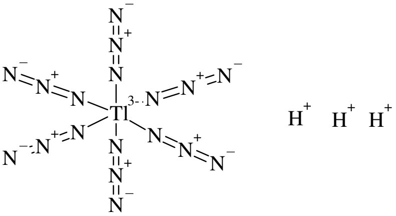
See Azidogermane: Fluorosilane

See other NON-METAL AZIDES

See related SILANES

4497. Hydrogen hexaazidothallate(III)

[63338-74-9] **$H_3N_{18}Tl$**



Krommes. P. *et al., J. Organomet. Chem.*, 1977, **131**, 418

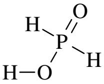
Not more than 200—500 mg portions of this extremely heat- and impact-sensitive explosive should be prepared.

See other N-METAL DERIVATIVES

See related METAL AZIDES

4498. Phosphinic acid ('Hypophosphorous acid')

[6303-21-5] **H_3O_2P**



1. Mellor, 1940, Vol. 8, Suppl. 3, 614
2. Albright and Wilson (Manufacturer's safety sheet)
3. *MARS Database*, 1998, short report 181

The explosion hazard associated with the usual laboratory preparation from white phosphorus and alkali may be avoided by an alternative method involving oxidation of phosphine with an aqueous iodine solution [1]. The commercial 50% solution reacts violently with oxidants. On heating, it decomposes rapidly above 100°C evolving phosphine, which is liable to explode with air. It is recommended it be kept below 50°C [2]. During vacuum concentration of a dilute solution on small industrial scale, a crust formed, overheated and decomposed, pressurising the system with phosphine which escaped and produced two explosions on mixing with air, causing modest damage to the factory installations [3].

Mercury(II) nitrate

See Mercury(II) nitrate: Phosphinic acid

Mercury(II) oxide MRH 0.71/86

Mellor, 1940, Vol. 4, 778

The redox reaction is explosive.

See other REDOX REACTIONS

Other reactants

Yoshida, 1980, 343

MRH values calculated for 6 combinations with various other materials are given.

See other INORGANIC ACIDS, REDUCANTS

4499. Phosphonic acid (Phosphorous acid)

[13598-36-2] **H_3O_3P**

1. Partington, 1946, 614
2. Albright and Wilson, (Manufacturer's safety sheet)

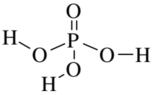
It decomposes at around 200°C with evolution of phosphine which may ignite [1]. Yellow deposits may form in aqueous solution which are spontaneously flammable on drying [2].

See Phosphorus trichloride: Carboxylic acids

See other INORGANIC ACIDS, REDUCANTS

4500. Orthophosphoric acid

[7664-38-2] **H_3O_4P**



(*MCA SD-7*, 1958); *NSC 674*, 1978; *HCS 1980*, 742, 743, *MCA SD-70*, 1958

Although it is not an oxidant, it is an active acid which, because of its low equivalent wt. and availability in high concentration and density (90% soln. is 50N), can develop a large exotherm on neutralisation. Handling precautions are detailed.

Chlorides, Steel

1. Piekarz, J., *Chem. in Can.*, 1961, **13**(4), 40—41
2. U.S. Dept of Energy, Office of Nuclear and Facility Safety, Operating Experience Summary 97-32, 1997.

Presence of traces of chloride ion in technical 75% phosphoric acid in a closed stainless steel storage tank caused corrosion and liberation of hydrogen which later exploded at a sparking contact [1]. Steel drums (presumably mild steel) into which phosphoric acid had been transferred, pressurised and burst within a day [2].

See other CORROSION INCIDENTS, GAS EVOLUTION INCIDENTS

Nitromethane

See Nitromethane: Acids, etc.

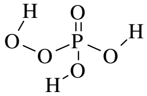
Sodium tetrahydroborate

See Sodium tetrahydroborate: Acids

See other INORGANIC ACIDS

4501. Peroxomonophosphoric acid

[13598-52-2] **H_3O_5P**



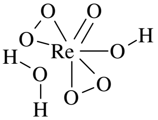
Coal, Potassium permanganate
See Potassium permanganate: Coal, etc.

Organic material
Castrantas, 1965, 5
The 80% solution causes ignition when dropped onto organic material.
See other INORGANIC ACIDS, PEROXOACIDS

Preparative hazard
See Hydrogen peroxide: Phosphorus(V) oxide

4502. Hydroxyaqua(oxo)diperoxorheniumVII

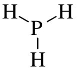
[ ] **H_3O_7Re**



Herrmann, W. A. *et al., Chem. Eur. J.*, 1996, **2**(2), 168
A highly explosive red/orange solid, obtained from rhenium trioxide and hydrogen peroxide reacting in hexamethylphosphoramide as solvent, was tentatively assigned this structure.
See other INORGANIC PEROXIDES

†4503. Phosphine

[7803-51-2] **H_3P**



HCS 1980, 745 (cylinder); *RSC Lab. Hazards Safety Data Sheet No. 49*^{0}, 1986

1. Rüst, 1948, 301
2. Sidgwick, 1950, 729
3. Mellor, 1940, Vol. 8, 811, 814
4. McKay, H. A. C., *Chem. & Ind.*, 1964, 1978
5. Anon., *Lab. Haz. Bull.*, 1982, (3), item 120
6. Green, A. R. *et al., Dev. Agric. Eng.*, 1984, **5** (Controlled Atmos. Fumig. Grain Storage), 433—449
7. Ethenakis, V. M. *et al., Sol. Cells*, 1987, **22**, 305—317

Liquefied phosphine (a mildly endothermic compound, ΔH_f° (g) +22.8 kJ/mol, 0.67 kJ/g) can be detonated by powerful initiation [1]. Pure phosphine does not spontaneously ignite in air below 150°C unless it is thoroughly dried, when it ignites in cold air. The presence of traces (0.2%) of diphosphane in phosphine as normally prepared causes it to ignite spontaneously in air, even at below —15°C [2]. Traces of oxidants promote pyrophoricity [3]. Phosphine, generated by action of water on calcium phosphide, was dried by passage through towers packed with the latter. Soon after refilling the generator (but not the towers) and starting purging with argon, a violent explosion occurred. This was attributed to the air, displaced from the generator by argon, reacting explosively with dry phosphine present in the drying towers, possibly catalysed by the orange-yellow polyphosphine formed on the surface of calcium phosphide. Fresh calcium phosphide in both generator and drying towers, with separate purging, is recommended [4]. During vacuum transfer of the supposedly pure gas, air leaked into the cold-trap system and caused an explosion [5]. Lower flammability limit of pure phosphine in moist air (0.39 vol% water vapour) at 1037 mbar was 2.1% at 10° and 1.85% at 50°C. Presence of ammonia may tend to reduce the limit value [6]. Potential hazards involved in use of phosphine in manufacture of photovoltaic cells are reviewed [7].

See Oxygen, below

See also Phosphonium iodide: Potassium hydroxide

Boron trichloride

See Boron trichloride: Phosphine

Dichlorine oxide MRH 5.36/84

See Dichlorine oxide: Oxidisable materials

Halogens MRH Chlorine 2.13/89

Mellor, 1940, Vol. 8, 812

Ignition occurs on contact with chlorine or bromine or their aqueous solutions.

Metal nitrates MRH Silver nitrate 3.77/87

Mellor, 1941, Vol. 3, 471; 1940, Vol. 4, 993

Passage of phosphine into silver nitrate solution causes ignition or explosion, depending on the gas rate. Mercury(II) nitrate solution gives a complex phosphide, explosive when dry.

Nitric acid MRH 7.78/74

See Nitric acid: Non-metal hydrides

Nitrogen trichloride MRH 3.64/91

Other reactants

Yoshida, 1980, 342

MRH values calculated for 10 combinations with oxidants are given.

Oxidants MRH values below reference

Mellor, 1940, Vol. 8, 811, 814

MRH Dinitrogen monoxide 6.99/84, dinitrogen trioxide 9.25/75, nitrogen oxide 9.71/78, nitrous acid 7.11/79

Pure phosphine is rendered pyrophoric by traces of dinitrogen trioxide, nitrous acid, or similar oxidant.

See Dichlorine oxide; Halogens; Metal nitrates; Nitric acid, all above, Oxygen, below

Oxygen

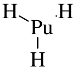
1. Fischer, E. O. *et al., Angew. Chem. (Intern. Ed.)*, 1968, **7**, 136
2. Mellor, 1971, Vol. 8, Suppl. 3, 281—282

Even small amounts of oxygen present in phosphine give an explosive mixture, in which autoignition occurs at low pressures [1]. The effects of other materials upon the explosive interaction have been studied [2].

See other ENDOTHERMIC COMPOUNDS, NON-METAL HYDRIDES

4504. Plutonium(III) hydride

[15457-77-9] **H_3Pu**



Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64

The hydride (and the metal) when finely divided are spontaneously flammable, and burning causes a specially dangerous contamination problem, in view of the radioctive and toxic hazards.

Water

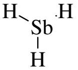
Bailar, 1973, Vol. 5, 150

Rapid addition of water often causes ignition of the hydride.

See other METAL HYDRIDES

†4505. Stibine

[7803-52-3] **H_3Sb**



Mellor, 1939, Vol. 9, 394

During evaporation of liquid stibine at —17°C, a relatively weak and isothermal explosive decomposition may occur. Gaseous stibine at ambient temperature may propagate an explosion from a hot spot on the retaining vessel wall, and it autocatalytically decomposes, sometimes explosively, at 200°C.

It is moderately endothermic (ΔH_f°(g) +145.2 kJ/mol, 1.16 kJ/g).

Ammonia

Mellor, 1939, Vol. 9, 397

A heated mixture explodes

Oxidants

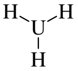
See Chlorine: Non-metal hydrides
Nitric acid: Non-metal hydrides
Ozone: Stibine

See other ENDOTHERMIC COMPOUNDS, METAL HYDRIDES

See related NON-METAL HYDRIDES

4506. Uranium(III) hydride

[13598-56-6] **H_3U**



Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64

The dry powdered hydride readily ignites in air.

Halocarbons

Bailar, 1973, Vol. 5, 150

Contact of the hydride with halogen-containing solvents may lead to explosive interaction.

Water

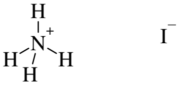
Bailar, 1973, Vol. 5, 150

Rapid addition of water often causes ignition of the hydride.

See other METAL HYDRIDES

4507. Ammonium iodide

[12027-06-4] **H_4IN**



Bromine trifluoride

See Bromine trifluoride: Ammonium halides

See related METAL HALIDES

4508. Ammonium iodate

[13446-09-8] **H_4INO_3**

Anon., *ABCM Quart. Safety Summ.*, 1955, **26**, 24

Violent decomposition occurred on touching with a scoop (which presumably was contaminated). A similar batch of material contained less than 100 ppm of periodate.

Other reactants

Yoshida, 1980, 375

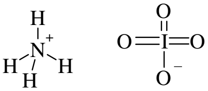
MRH values calculated for 15 combinations with oxidisable materials are given.

See other IODINE COMPOUNDS

See related METAL OXOHALOGENATES

4509. Ammonium periodate

[13446-09-8] **H_4INO_4**



1. Anon., *Chem. Eng. News*, 1951, **29**, 1770
2. Mellor, 1940, Vol. 2, 408

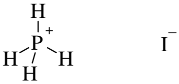
It exploded while being transferred by scooping [1]. The sensitivity towards heat, but not abrasive impact, was known previously [2].

See other IODINE COMPOUNDS

See related METAL OXOHALOGENATES

4510. Phosphonium iodide

[12125-09-6] **H_4IP**



Oxidants

Mellor, 1947, Vol. 8, 827

Bromates, chlorates or iodates ignite in contact with phosphonium iodide at ambient temperature if dry, or in presence of acid to generate bromic acid, etc. Ignition also occurs with nitric acid, and reaction with dry silver nitrate is very exothermic. Interaction with antimony pentachloride at ambient temperature proceeds explosively.

See other REDOX REACTIONS

Potassium hydroxide

Anon., *Univ. Safety Assoc., Safety Newsletter*, 1983—1984

Phosphine, generated by action of the alkali on phosphonium iodide, was shown to be pure by mass spectrometry. During a second preparation, an air leak developed during cold-trap transfer and an explosion occurred. Presence of diphosphane was suspected.

See Phosphine (reference 2)

Water

See Phosphorus: Hydriodic acid

See other REDUCANTS

4511. Potassium tetrahydrozincate

[34324-17-9] **H_4K_2Zn**

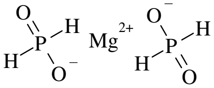
Ashby, E. C. *et al., Inorg. Chem.*, 1971, **10**, 2486

Extremely reactive, pyrophoric in air.

See other COMPLEX HYDRIDES

4512. Magnesium phosphinate

[7783-17-7] **$H_4MgO_4P_2$**



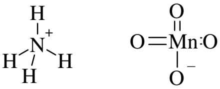
Mellor, 1940, Vol. 8, 885

On heating it evolves phosphine which ignites in air.

See other METAL PHOSPHINATES, REDUCANTS

4513. Ammonium permanganate

[13446-10-1] **H_4MnNO_4**



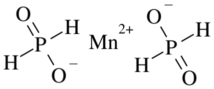
1. Mellor, 1942, Vol. 12, 302
2. Pavlychenko, M. M. *et al., Chem. Abs.*, 1962, **57**, 2897e

The dry material is friction-sensitive and explodes at 60°C in air [1]. Under vacuum, decomposition becomes explosive above 100°C, and sparks will also initiate decomposition.

See other OXIDANTS, OXOSALTS OF NITROGENOUS BASES (reference 1)

4514. Manganese(II) phosphinate

[10043-84-2] **$H_4MnO_4P_2$**



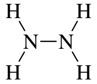
Mellor, 1940, Vol. 8, 889

It explodes above 200°C.

See other HEAVY METAL DERIVATIVES, METAL PHOSPHINATES, REDUCANTS

†4515. Hydrazine

[302-01-2] **H_4N_2**



HCS 1980, 536 (anhydrous), 537 (hydrate); *RSC Lab. Hazard Data Sheet No. 14*, 1983

1. Troyan, J. E., *Ind. Eng. Chem.*, 1953, **45**, 2608
2. Day, A. C. *et al., Org. Synth.*, 1970, **50**, 42
3. *491M*, 1975, 199
4. Mitchell, J. W., *Anal. Chem.*, 1980, **52**, 774—776
5. Bellerby, J. M. *et al., Chem. Abs.*, 1982, **96**, 222535
6. Bunker, R. L. *et al., Prog. Astronaut. Aeronaut.*, 1991, **133**, 324
7. *Hydrazine and its Derivatives*, Schmidt, F. W., New York, Wiley, 1984

It is rather endothermic (ΔH_f° (l) +50.4 kJ/mol, 1.57 kJ/g) and readily decomposed.

Hydrazine is an endothermic compound and the vapour is exceptionally hazardous in that once it is ignited, it will continue to burn by exothermic decomposition in complete absence of air or other oxidant [1]. Distillation of anhydrous hydrazine (prepared by dehydrating hydrazine hydrate with solid sodium hydroxide) must be carried out under nitrogen to avoid the possibility of an explosion if air is present [2]. If spread with an extended surface (as a thin film, or absorbed on porous or fibrous material), anhydrous hydrazine may autoxidise with sufficient heat generation and retention to cause ignition. Presence of traces of metal catalysts (as in some cellulosic materials) will greatly accelerate this effect [3]. Procedures for safe handling and purification of aqueous hydrazine solutions are detailed [4], and autoxidation processes of hydrazine and its methylated derivatives have been reviewed [5]. The mechanism by which hydrazine can be detonated during pumping operations has been studied [6]. A comprehensive monograph includes sections on decomposition and other hazard-related aspects of the preparation and applications of hydrazine [7].

See Barium oxide, below
See Cotton waste, below
See also Heavy metals, below
See also Metal catalysts, below

Barium oxide, or Calcium oxide

1. Gmelin, 1935, Syst. 4, 318
2. *ABCM Quart. Safety Summ.*, 1950, **21**, 18

The residue from dehydrating hydrazine with barium oxide slowly decomposes exothermically in daylight and finally explodes [1]. Dehydration of 95% hydrazine by boiling with calcium oxide under nitrogen caused violent explosions on 2 occasions. It was concluded that use of calcium or barium oxides for this purpose is potentially dangerous, and that boiling under reduced pressure may be advisable to lower the liquid temperature. General precautions in handling hydrazine are discussed [2].

See Sodium hydroxide, below

Benzeneseleninic acid or anhydride

See Benzeneseleninic acid: Hydrazine derivatives

Calcium

Hydrazine and its Derivatives, Schmidt, F. W., New York, Wiley, 1984, 75

Use of excess calcium metal, or its solution in ammonia (presumable calcamide) to dry hydrazine leads to formation of calcium hydrazide and explosion. Calcium hydride and carbide are, apparently, safe drying agents

See METAL HYDRAZIDES

Carbon dioxide, Stainless steel

Bellerby, J. M., *J. Haz. Mat.*, 1983, **7**, 187—197

The rate of decomposition of hydrazine in stainless steel vessels (which is accompanied by corrosion) is directly proportional to carbon dioxide concentration over 20 ppm and below 250 ppm. The species responsible for the catalytic decomposition is not one of the expected corrosion products, iron(II) carbazate or its nickel or chromium(II) analogues.

See other CATALYTIC IMPURITY INCIDENTS, CORROSION INCIDENTS

1-Chloro-2,4-dinitrobenzene

See 1-Chloro-2,4-dinitrobenzene: Hydrazine hydrate

2-Chloro-5-methylnitrobenzene

See 2-Chloro-5-methylphenylhydroxylamine

Cotton waste, Heavy metals

Orme, R. J., private comm., 1980

In a factory manufacturing organo-iron and organo-manganese catalysts, use of cotton waste to mop up a spill of dilute hydrazine solution led to a spontaneous fire later. The fire was attributed to onset of rapid metal-catalysed decomposition of the hydrazine after sufficient water had evaporated from the waste, the traces of heavy metals originating from dust contamination, etc.

See Metal catalysts, below

Dicyanofurazan

See Dicyanofurazan: Nitrogenous bases

(Difluoroamino)difluoroacetonitrile

See (Difluoroamino)difluoroacetonitrile: Hydrazine

Dinitrogen oxide

See Dinitrogen oxide: Hydrazine

Iodine pentoxide

Speeds, S. J. *et al.*, US Pat. Appl. 844 082, 1977

The oxide is used to effect rapid decomposition of hydrazine in a high-temperature gas generator which produces exit pressures (of nitrogen, hydrogen and ammonia) of 550 bar.

Metal catalysts

1. Mellor, 1940, Vol. 8, 317: 1967, Vol. 8, Suppl. 2.2, 83
2. Audrieth, L. F. *et al., Ind. Eng. Chem.*, 1951, **43**, 1774
3. Troyan, J. E., *Ind. Eng. Chem.*, 1953, **45**, 2608
4. Blumenthal, J. L. *et al.*, US Pat. 3 846 339, 1974
5. Rao, K. R. *et al., Trans. Powder Metall. Assoc. India*, 1975, **2**, 64—66
6. Armstrong, W. E. *et al.*, US Pat. 4 124 538, 1978
7. Bellerly, J. M., *J. Haz. Mat.*, 1986, **13**(1), 57—60

In contact with metallic catalysts (platinum black, Raney nickel) hydrazine is catalytically decomposed, yielding ammonia, hydrogen and nitrogen. With conc. hydrazine the reaction may be violent, and the ammonia and hydrogen evolved could be ignited by particles of dry catalyst [1]. Measures to prevent autoxidation of hydrazine catalysed by traces of copper are discussed, including displacement of air from transportation containers with nitrogen [2]. Catalytic decomposition is effected by iron oxide, molybdenum-stabilised stainless steel, molybdenum and its oxides, and finely divided solids. Handling procedures are discussed [3]. A rhenium—alumina catalyst causes immediate ignition of undiluted hydrazine [4]. The effect upon ignition delay of thermal treatment and particle size of powdered transition metal catalysts has been studied [5]. Iridium or iridium—ruthenium on alumina also effect catalytic decomposition of hydrazine [6]. Soluble chromium and/or manganese species do not increase the rate of decomposition of anhydrous hydrazine, but presence of traces of acid as well leads to significantly increased rates [7].

Metal salts

1. Mellor, 1941, Vol. 7, 430; 1940, Vol. 8, 318; 1967, Vol. 8, Suppl. 2.2, 882
2. Traynham, J. G. *et al., J. Org. Chem.*, 1967, **32**, 3285
3. McCoy, P. O., *Chem. Eng. News*, 1970, **48**(48), 9

Several of its complexes with metallic salts are unstable, including those of basic cadmium perchlorate (highly explosive), cadmium nitrite (explosive), copper chlorate (explodes on drying without heat), manganese nitrate (ignites at 150°C), mercury(I) chloride, mercury(II) chloride, mercury(I) nitrate, mercury(II) nitrate (all are explosive) and tin(II) chloride (explodes on heating): other examples are given [1]. There is a published method for reducing *cis-trans*-cyclododecadiene to the *cis*-monoene with diazene ('diimide') generated in situ from hydrazine, copper(II) salts and air [2]. During a modified reaction sequence using crude diene, much sludge containing polymer, copper(II) acetate and hydrazine was produced. When filtered off in air, the sludge heated and eventually glowed. Use of purified diene and filtration under nitrogen avoids the problem [3].

See Trihydrazinealuminium perchlorate

See also AMMINEMETAL OXOSALTS

Methanol, Nitromethane

See Nitromethane: Hydrazine, Methanol

Molybdenum sulfide

Peng, Y. *et al., Chem. Lett.*, 2001, (8), 772

Some forms of molybdenum sulphide catalyse the violent decomposition of hydrazine hydrate.

Other reactants

Yoshida, 1980, 283

MRH values calculated for 16 combinations with oxidants are given.

Oxidants MRH values below references show % of oxidant

1. *Haz. Chem Data*, 1975, 166
2. Mellor, 1941, Vol. 3, 137; 1940, Vol. 8, 313—319; 1943, Vol. 11, 234
3. *ASESB Op. Incid. Rept. No. 105*
4. Troyan, J. E., *Ind. Eng. Chem.*, 1953, **45**, 4608
5. Wannagat, U. *et al., Monatsh. Chem.*, 1969, **97**, 1157—1162
6. Ephraim, 1939, 651

MRH Ammonium nitrate 3.97/84, chromium trioxide 3.01/81, hydrogen peroxide 6.36/68, nitric acid 5.84/61, potassium dichromate 1.59/tr., sodium chlorate 6.07/69, sodium nitrate 3.18/68

Hydrazine is a powerful, endothermic reducing agent, and its interaction with oxidants may be expected to be violent if unmoderated, as in rocket propulsion systems (often hypergolic). Mixtures of hydrazine vapour with air are explosive over a very wide range (4.7—100%) and ignition temperature can be very low (24°C on a rusty iron surface). When mixed with, or spilt on, highly porous materials (asbestos, cloth, earth, wood), autoxidation in air may proceed fast enough to cause ignition. Contact with hydrogen peroxide or nitric acid may cause ignition with conc. reagents and with dinitrogen tetraoxide is hypergolic [1]. Contact with chromate salts or chromium trioxide causes explosive decomposition. Copper oxide or lead oxide cause a vigorous decomposition, while dropping hydrazine hydrate on to mercury oxide can cause an explosion. This may be owing to known oxidation of hydrazine to hydrogen azide by two electron transfer, and formation of explosive mercury azide [2]. Contact of hydrazine with the explosive *N*,2,4,6-tetranitroaniline caused ignition [3]. Contact of iron oxide, chlorates or peroxides may lead to violent reactions [4]. The ignition delay with fuming nitric acid was 8 ms, explosion also occurring [5]. Contact with potassium permanganate leads to explosion [6].

See Lithium perchlorate: Hydrazine
Potassium peroxodisulfate: Hydrazine, etc.
Silver(I) oxide: Ammonia, etc.
Sodium perchlorate: Hydrazine MRH 5.86/65
'Trioxygen difluoride': Various materials

See N-HALOIMIDES, ROCKET PROPELLANTS

See also SILYLHYDRAZINES: Oxidants

Phosphorus tribromide

See Phosphorus tribromide: hydrazine derivatives

Potassium

Gmelin, 1935, Syst. 4, 318

Explosive interaction.

See Sodium hydrazide

Rust

MCA Case History No. 1893

Use of rusty tweezers, rather than the glass rod specified to handle specimens being immersed in hot 64% hydrazine, caused the hydrazine vapour to ignite.

Ruthenium(III) chloride

Allen, A. D. *et al., Inorg. Synth.*, 1970, **12**, 3

During the preparation of pentaamminedinitrogenruthenium(II) solutions, the initial gas producing reaction is so vigorous that increase in scale above that described (9 mmol) is not advised.

See Metal catalysts, above

See Pentaamminechlororuthenium chloride: Sodium azide

Silver compounds MRH Silver nitrate 3.10/78

Anon., *CISHC Chem. Safety Summ.*, 1978, **49**(194), 29

For analysis, a silver-containing solution was made alkaline with 25% sodium hydroxide solution and filtered, then the precipitate was washed with ammonium hydroxide to redissolve the silver. Hydrazine (as sulfate) was added to precipitate the silver, and when the mixture was heated, an explosion occurred. This could have been caused by precipitation of explosive silver nitride, rapid catalytic decomposition by silver compounds of the hydrazine salt, and/or ignition of the hydrogen evolved.

Sodium

See Sodium: Hydrazine

Sodium hydroxide

1. Anon., *Univ. Safety Assoc., Safety News*, 1978, (10), 12
2. Day, A. C. *et al., Org. Synth.*, 1970, **50**, 42

While drying hydrazine over sodium hydroxide pellets, explosive decomposition occurred, spraying molten sodium hydroxide around. This was attributed to possible leakage of air into the evacuated flask.

Thiocarbonyl azide thiocyanate

See Thiocarbonyl azide thiocyanate: Ammonia, etc.

Titanium compounds

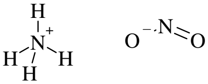
Bains, M. S., *Can. J. Chem.*, 1966, **44**, 534—538

Interaction of anhydrous hydrazine and titanium isopropoxide is explosive at 130°C in absence of solvent. Evaporation of solvent ether from the reaction product of tetrakis(dimethylamino)titanium and anhydrous hydrazine caused an explosion, attributed to formation and ignition of dimethylamine. *N*-Metal derivatives may also have been formed.

See other NON-METAL HYDRIDES, REDUCANTS

4516. Ammonium nitrite

[13446-48-5] **$H_4N_2O_2$**

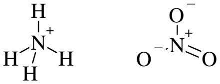


See Nitric Acid: Manufacture Hazard

See entry NITRITE SALTS OF NITROGENOUS BASES

4517. Ammonium nitrate

[6484-52-2] **$H_4N_2O_3$**



FPA H33, 1975; *HCS 1980*, 147

1. Federoff, 1960, 35
2. Urbanski, 1965, Vol. 2, 460
3. Popper, H., *Chem. Eng.*, 1962, **70**, 91
4. Sykes, W. G. *et al., Chem. Eng. Progr.*, 1963, **59**(1), 66
5. Yoshida, T., private comm., 1983
6. Urben, P. G., *Loss Prev. Bull.*, 1992, **108**, 31
7. Mellor, 1964, Vol. 8, Suppl. 1, 543
8. *MCA Guide*, 1972, 308
9. Croysdale, L. G. *et al., Chem. Eng. Progr.*, 1965, **61**(1), 76
10. *MCA Case History No. 873*
11. Bailar, 1973, Vol. 2, 317
12. Vakhrushev, Yu. A. *et al., Chem. Abs.*, 1975, **82**, 113745
13. Pascal, 1956, Vol. 10. 216
14. Rozman, B. Yu., *Chem. Abs.*, 1960, **54**, 12587c
15. Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345—351
16. Freeman, R., *Chem. Eng. Progr.*, 1975, **71**(11), 71—74
17. David, A. *et al., Hydrocarbon Process.*, 1978, **57**(11), 149—175
18. Shah, K. D., *Fert. Sci. Tech. Ser.*, 1985, **4**, 261—273
19. Kirschner, E. *Chem. Eng. News*, 1994, **72**(51), 4; *ibid.*, **73**(37), 7
20. Anon., *Chem. Eng. News*, 1996, **74**(5), 11
21. Wiswesser, W. J., private comm., 1988
22. Anon., *Fire Prevention*, 1990, (231), 40
23. Li, R. *et al., Arch. Combust.*, 1988, **8**(1), 65—70
24. Buczkowski, D. *et al., Chem Abs.*, 1996, **125**, 176043e
25. USA Environmental Protection Agency, EPA 550-F-97-002d
26. Lunelli, B., *Chem. Brit.*, 2002, **38**(7), 18
27. Anon., *Chem. Brit.*, 2002, **38**(9), 9

28. http://aria.environnement. gouv fr, 2001, Inventaire des Accidents Technologiques et Industriels, (25/09/2001); Accidents Impliquant des Nitrates d'Ammonium.
29. Lunelli, B. *Chem. & Ind. (Milan)*, 2003, **85**(4), 59
30. Shockey, D. A. et al., Engineering Failure Analysis, 2003, 10(5), 627
31. Dechy, N. *et al., J. Haz. Mat.*, 2004, **111**(1-3), 131

The decomposition, fire and explosion hazards of this salt of positive oxygen balance have been adequately reviewed [1-4]. In the absence of impurities it is difficult, but not impossible, to cause ammonium nitrate to detonate. Use of explosives to break up the caked double salt, ammonium nitrate—ammonium sulfate (2:1), caused a 4.5 Mkg dump to detonate [4], even though some 45% of ammonium sulfate was present, effectively as a diluent, in the salt. Although the explosion tests available in 1921 did not give positive results for the nitrate—sulfate salt, it has more recently been shown, using the BAM 50/60 steel tube test, that it will explode [5]. The ammonium sulphate is unlikely to be totally inert, having a negative enthalpy of decomposition to steam, nitrogen and sulfur, which last is capable of oxidation to sulfur dioxide, bringing the double salt into oxygen balance [6]. The effect of various impurities and additives on the thermal stability of ammonium nitrate has been widely studied [1,2,7]. Impure ammonium nitrate now constitutes more than 95% of all civil explosives used in the USA. A few incidents involving explosive decomposition of aqueous solutions of the salt during evaporation [8], or transfer operations (some in presence of oil) have been recorded [9]. Flame cutting a mild steel pipe blocked by the solid (impure) salt caused it to explode [10]. During preparation of dinitrogen oxide by the exothermic pyrolysis of the nitrate at 170°C, the temperature must not be allowed to exceed 250°C, as explosion may occur [11].

The thermal stability of ammonium nitrate solutions is decreased by presence of sodium 1,1'-methylenebis(6-naphthalenesulfonate) at 0.15%, but zinc oxide or zinc sulfate—apatite mixtures act as stabilisers [12]. Presence of ammonium chloride (0.1%) causes thermal decomposition to become violent around 175°C, and some chlorine is evolved [13]. Magnesium nitrate is claimed to significantly desensitise ammonium nitrate [24]. The parameters involved in the self-ignition of the nitrate during storage or transport are described, and a mechanism for instantaneous decomposition is proposed [14]. The factors affecting potentially explosive decomposition in bulk storage of the salt are discussed, and steady state thermal explosion theory is applied to the prediction of critical masses in relation to temperature in bulk storage. Application of the results to current storage practice is also discussed [15]. A detailed account of the investigation of a fire and explosion (basically unexplained) involving some 5 t of nitrate of a 14 kt warehouse stock has been published [16]. A 2-stage production process is designed to minimise danger of decomposition of the salt [17]. Accidents involving ammonium nitrate and the factors causing them are reviewed, and procedures for manufacturing, handling, storage and transportation are discussed [18]. A large explosion, probably of some tons TNT equivalent with several fatalities, during concentration of ammonium nitrate solution for fertiliser manufacture is discussed. There had been 750 tons of the nitrate present, the initiation mechanism is disputed though acidity, impurities, heat and lack of supervision were involved [19,20,30]. This incident has triggered the issue of a summarised report on ammonium nitrate and its hazards [25]. Road trailers laden with 14 t and 7 t of nitrate were involved in a fire and 3 subsequent detonations [21]. Another account of this incident makes it clear that it was, for the most part, ammonium nitrate/fuel oil (ANFO) explosive rather than the pure nitrate which exploded [22]. During pneumatic pipeline conveyance of the powdered salt, electrostatic generation is unlikely to be a problem under smooth flow conditions. However, the possibility of fast charge accumulation if flow discontinuities arise must not be overlooked [23]. An explosion at an ammonium nitrate plant in Toulouse, with a TNT equivalence of many decatonnes, generated the suggestion that initiation might be due to the change of a metastable crystal form to a lower energy, but more bulky, polymorph in confined space or the heart of a storage heap. Ammonium nitrate is known to be polymorphic [26,29]. It is hypothesised that the Toulouse explosion may have been initiated by storage of incompatible sodium dichloroisocyanurate in the same warehouse. The stock which exploded was only in the low hectotonne range, smaller than previous spontaneous explosions and may cause a reduction in permissible storage weights to 150 tonnes [27]. The Toulouse explosion rapidly produced a French history of explosions and fires associated with ammonium nitrate, some only loosely so [28]. The exact cause was still under debate three years later [31].

See also

Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide

Acetic acid MRH 3.30/16

von Schwartz, 1918, 322

Conc. mixtures ignite on warming.

Acetic anhydride, Hexamethylenetetramine acetate, Nitric acid

See Nitric acid: Acetic anhydride, Hexamethylenetetramine acetate

Alkali metals MRH Sodium 4.15/36

Mellor, 1964, Vol. 8, Suppl. 1, 546

Sodium progressively reduces the nitrate, eventually forming a yellow explosive solid, probably sodium hyponitrite.

Aluminium, Calcium nitrate, Formamide

See Calcium nitrate: Aluminium, etc.

Ammonia

Kohczkowski, A. *et al., J. Chem. Technol. Biotechnol.*, 1981, **31**, 327—332

Depending on the conditions, presence of free ammonia in ammonium nitrate may either stabilise, or tend to destabilise, the salt.

Ammonium chloride, (Barium nitrate), Water, Zinc

1. Bailey, P. S. *et al., J. Chem. Educ.*, 1975, **52**, 525
2. Jackson, H., *Spectrum*, 1969, **7**(2), 82
3. Bodner, G. M., *J. Chem. Educ.*, 1985, **62**(12), 1106

Addition of water to an intimate mixture of zinc powder and the salts causes spontaneous ignition [1], and a mixture of ammonium nitrate and ammonium chloride (9:1) sprinkled with zinc dust ignites vigorously when moistened [2]. Premature spontaneous ignition of the mixture was attributed to absorption of moisture by the hygroscopic salt mixture [3].

See Metals, below

See other REDOX REACTIONS

Ammonium phosphate, Potassium sulfate

Gryzlov, L. D. *et al., Chem. Abs.*, 1986, **104**, 185477

During manufacture of 26/16/10 N/P/K fertiliser by ammoniation of nitric—phosphoric acid mixtures, followed by concentration, addition of potassium sulfate, then granulation at up to 250°C, the possibility of a thermal explosion exists. Kinetic studies showed that 240°C appears to be a safe granulation temperature, but that changes in the composition and pH of the mixture may decrease this critical temperature.

Ammonium sulfate, Potassium

Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549

Ammonium nitrate containing the sulfate readily explodes on contact with potassium or its alloy with sodium.

Calcium superphosphate, Lignin, Phosphoric acid, Urea

Dobreva, Ts. *et al., Chem. Abs.*, 1988, **109**, 37213

The products of thermal decomposition of organic—mineral fertiliser mixtures were studied by IR spectroscopy, and implications for fire and explosion hazards considered.

See Urea, below

Charcoal, Metal oxides MRH Carbon 3.64/7

Herbst, H., *Chem. Ztg.*, 1935, **59**, 744—745

The pelleted explosive (‘ammonpulver’, containing 10% charcoal) normally ignites at 160—165°C, but presence of rust, or copper oxide or zinc oxide lowers the temperature to 80—120°C.

See Non-metals, below

Chloride salts

1. Pascal, 1956, Vol. 10, 216
2. Pany, V. *et al., Chem. Abs.*, 1976, **85**, 56018

The nitrate containing 0.1% of ammonium chloride decomposes vigorously below 175°C [1]. Presence of 0.1% of calcium chloride or iron(III) chloride in the nitrate lowers its initiation temperature sufficiently to give violent or explosive decomposition. Thermal analysis plots for aluminium chloride, calcium chloride and iron(III) chloride are given [2].

Copper iron(II) sulfide

Kuznetsov, G. V. *et al., Chem. Abs.*, 1975, **82**, 75133

During preparations for blasting the sulfide mineral copper pyrites, ammonium nitrate-based blasting cartridges exploded prematurely in the blast holes. This was attributed to exothermic interaction of acid ground-water with the sulfide—oxidant combination.

See Metal sulfides, below

Cyanoguanidine

See Cyanoguanidine: Oxidants

Fertiliser materials

Davies, R. O. E. *et al., Ind. Eng. Chem.*, 1945, **37**, 59—63

Mixtures of ammonium nitrate, superphosphate and organic materials stored in bulk may ignite if the internal temperature exceeds 90°C. This is owing to the free acid in the superphosphate, and may be prevented by neutralisation with ammonia.

See also FERTILISER

Hydrocarbon oils MRH Hexane 3.80/5, Toluene 3.80/7

Goffart, P., *Chem. Abs.*, 1975, **82**, 61420

Detonability of several ammonium nitrate-based fertilisers, with or without the addition of fuel oil, was studied.

Metal salts

1. Glazkova, A. P., *Chem. Abs.*, 1970, **73**, 132646
2. Rosser, W. A. *et al., Trans. Faraday Soc.*, 1964, **60**, 1618—1625

Catalytic effects on the thermal decomposition and burning under nitrogen of the nitrate were determined for ammonium dichromate, potassium dichromate, potassium chromate, barium chloride, sodium chloride and potassium nitrate. Chromium(VI) salts are most effective in decomposition, and the halides salts during burning of the nitrate [1]. The effect of chromium compounds soluble in the molten nitrate, all of which promote decomposition of the latter, was studied (especially using ammonium dichromate) in kinetic experiments [2].

Metal sulfides

Proc. 13th Symp. Explos. Pyrotech., 1986, **VII**, 1—7; (*Chem. Abs.*, 1989, **110**, 98227s)

In presence of sulfide ores, specifically pyrites, explosives containing ammonium nitrate may undergo runaway reaction, leading to detonation at temperatures below 40°C if pH is less than 2. The reaction is acid catalysed.

Metals MRH Aluminium 8.49/25, lead 1.38/56, magnesium 8.79/31, sodium 4.15/36, zinc 3.22/tr.

1. Mellor, 1964, Vol. 8, Suppl. 1, 543—546
2. Soda, N. *et al., Chem. Abs.*, 1969, **70**, 49151
3. Peterson, W. S. *Light Met.* (Warrendale, Pa) 1995, 899

Many of the following powdered metals reacted violently or explosively with fused ammonium nitrate below 200°C: aluminium, antimony, bismuth, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, tin, zinc; also brass and stainless steel. Mixtures with aluminium powder are used as the commercial explosive Ammonal. Sodium reacts to form the yellow explosive compound sodium hyponitrite, and presence of potassium sensitises the nitrate to shock [1]. Shock-sensitivity of mixtures of ammonium nitrate and powdered metals decreases in the order titanium, tin, aluminium, magnesium, zinc, lead, iron, antimony, copper [2]. Contact between molten aluminium and the salt is violently explosive, apparently there is a considerable risk of this happening in scrap remelting [3].

See Ammonium sulfate, etc., above
Aluminium: Ammonium nitrate
Potassium: Nitrogen-containing explosives

Nitric acid
Rubtsov, Yu. I. *et al., Chem. Abs.*, 1987, **106**, 158775
In the context of safety of the process of neutralisation of nitric acid with ammonia, the effects of temperature (160—230°C), pressure (2.3—9.8 bar), and concentrations of ammonium nitrate (86—94%) and of nitric acid (0—4%) upon decomposition rate were studied.
See Nitric acid: Manufacture Hazard

Non-metals MRH Carbon 3.64/7, phosphorus (y) 4.60/14
Mellor, 1940, Vol. 2, 841—842; 1946, Vol. 5, 830
The powdered salt in admixture with charcoal explodes at 170°C, or the solid salt on contact with glowing charcoal. Phosphorus ignites on the fused salt.
See Sulfur, below
See also Phosphorus: Nitrates

Organic fuels MRH values below references
1. Sykes, W. G. *et al., Chem. Eng. Progr.*, 1963, **59**(1), 66
2. Urbanski, 1965, Vol. 2, 461
3. Bernoff, R. A. *et al.*, US Pat. 3 232 940, 1969

MRH Acetone 3.77/8, aniline 3.77/8, carbon disulfide 3.26/11, ethanol 3.68/9, ethylene glycol 3.56/14

In a review of ammonium nitrate explosion hazards, several incidents involving mixtures of this positive oxygen balance material with various organic materials were analysed [1]. In general, fire incidents involving ammonium nitrate admixed with 1% of wax, oil, or stearates (as anti-caking additives) tended more towards explosion than the pure salt, although the degree of confinement is also important [1,2]. The ease of detonation of mixtures is much greater when 2-4% of oil is present, and such mixtures are used as commercial explosives [2]. The preparation of ammonium nitrate—fuel systems at a molecular level is covered by the patent, which describes several alkylammonium nitrates as high-energy materials [3].

Other reactants
Yoshida, 1980, 190
MRH values calculated for 19 combinations with oxidisable materials are given.

Potassium nitrite
Mellor, 1940, Vol. 2, 842
Contact of the solid nitrate with fused nitrite causes incandescence.
See NITRITE SALTS OF NITROGENOUS BASES

Potassium permanganate
See Potassium permanganate: Ammonium nitrate

Sawdust
Biasutti, 1981, 151

A violent explosion in an ammonium nitrate store with sawdust-covered floors (to absorb spillage and prevent sparks) was attributed to local decomposition of the moist nitrate-containing sawdust, leading to temperature rise and spontaneous ignition. The observation of red-brown fumes just before the explosion supports this hypothesis.

Sugar

Gonzalez, M. M., *Chem. Abs.*, 1981, **65**, 83230

Mixtures of the salt with sugar syrup are effective explosives.

Sulfide ores

1. Liao, M. *et al., Proc. 13th Symp. Explos. Pyrotech.*, 1988, VII.1—VII.7
2. Derzhavets, A. S. *et al., Chem. Abs.*, 2004, **141**, 336593v

The main factors leading to spontaneous explosions of blasting explosives in sulfide ore mines are identified as presence of ammonium nitrate, presence of pyrites and their weathering products, as well as the pH and temperature. At pH below 2, the critical temperature for spontaneous explosion may be lower than 40° [1,2].

Sulfur

1. Mason, C. M. *et al., J. Agric. Food Chem.*, 1967, **15**, 954
2. Prugh, R. W., *Chem. Eng. Progr.*, 1967, **63**(11), 53—55

The fire risks of nitrate—sulfur mixtures have been discussed [1], and explosion risks assessed by DTA [2].

Trinitroanisole

Biasutti, 1981, 54

A mixture of ammonium nitrate and 2,4,6-trinitroanisole, prepared as an explosive by mixing the hot components, ignited spontaneously and later exploded violently.

Urea

1. Croysdale, L. C. *et al., Chem. Eng. Progr.*, 1965, **61**(1), 72
2. Anderson, J. F., *Safety Air Ammon. Plants*, 1967, **9**, 70—71
3. Leach, J. W., *Rept. AD-A075338*, Richmond (Va.), USNTIS, 1979
4. Perbal, G., *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 2, M1—M19, Rugby, IChE, 1983
5. Rubstov, Yu. I. *et al., Chem. Abs.*, 1988, **108**, 137111

Conc. solutions of ammonium nitrate and urea exploded during large-scale mixing operations. Although the cause was not established, the hazards of these operations were discussed in relation to the circumstances [1]. A further explosion under similar circumstances was reported [2]. Some of the liquid streams involved in preparation of nitroguanidine, which are somewhat similar to those in the present process, are detonable if less than 25% of water is present in the solutions. Thermal characteristics and detonation data were developed for the nitroguanidine process and that to produce guanidinium nitrate [3]. The circumstances of the 3 explosions [1,2] have been reviewed and detailed experimental work has confirmed that the solutions (54—46% ammonium nitrate, 35—39% urea and 15—20% water) cannot be detonated. However, dehydration of the solution gives a solid residue capable of deflagration at 240°C, and the residue from prolonged heating at 158°C is capable of detonation. It is concluded that the explosions were most likely caused by leakage and dehydration in the lagging of the steam-traced pipelines at 158°C, slow development of the unstable product and of a hot spot, with eventual initiation of detonation. Any traces of urea nitrate would not have contributed significantly to the events [4]. There is no danger of violent reaction as long as the components remain in solution. Processing temperatures should not exceed 120°C [5].

Water

Kolaczkowski, A. *et al., Chem. Abs.*, 1982, **97**, 78074

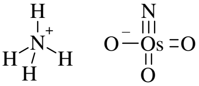
Hot aqueous solutions of the nitrate of above 50% concentration may decompose explosively under adiabatic conditions and under conditions of confinement (small, or no vents). A 9 m^3 tank of 85% solution also containing 0.9% of nitric acid and 0.2% of chloride ion (which catalyses decomposition) at 110°C exploded powerfully.

See other OXIDANTS, OXOSALTS OF NITROGENOUS BASES

See related METAL NITRATES

4518. Ammonium nitridoosmate

[22493-01-2] **$H_4N_2O_3Os$**



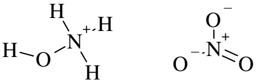
Mellor, 1942, Vol. 15, 727

It decomposes explosively at 150°C, like the barium salt.

See related NITRIDES

4519. Hydroxylaminium nitrate

[13465-08-2] **$H_4N_2O_4$**



1. Mellor, 1940, Vol. 8, 303
2. Kirk-Othmer, 1981, **16**, 179
3. Asaki, A., *Chem. Abs.*, 1983, **98**, 48238
4. Van Disk, C. A., *Chem. Abs.*, 1984, **100**, 70566
5. Sugikawa, S. *et al., JAERI-Conf.* 2002, (2002-004), 475 Jap. Atom. Energ. Inst.
6. U.S. DOE, Accident Investigation Report, DOE/RL-97-59, 1997; DOE EH-0555, 1998

The redox salt which decomposes at 100°C, evolving nitrogen and oxygen [1] is overall an oxidant but has been used as a reducant in actinide processing [2]. Even in the absence of actinides dilute solutions for this may concentrate by evaporation of watrer until there is an autocatalytic runaway. A widely publicised explosion from this cause (there have been others) generated official reports [6]. Stability studies

show solutions destabilised by nitric acid and iron, also on standing when slow decomposition releases nitric acid [5]. It has been used as a missile monopropellant [3], and also as an oxidant, with its isopropyl derivative as the fuel [4].
See also NUCLEAR WASTES
See other HYDROXYLAMINIUM SALTS

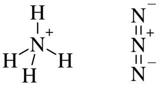
Amine nitrates
Klein, N., *Progr. Astronaut. Aeronaut.*, 1988, **109**(Gun Propell. Technol.), 473—497
The use of aqueous mixtures of hydroxylammonium nitrate with various butylammonium nitrates as gun propellants is reviewed.
See other OXOSALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

4520. Tetrahydroxotritin(2+) nitrate ('Basic stannous nitrate')
[73593-33-6] (ion) **$H_4N_2O_{10}Sn_3$**

1. Anon., *J. Soc. Chem. Ind.*, 1922, **41**, 423—434R
2. Donaldson, J. D. *et al., J. Chem. Soc.*, 1961, 1996

An explosion in flour-bleaching operations was attributed to violent decomposition of the basic nitrate [1], which is an impact-, friction- and heat-sensitive explosive [2]. The instability is associated with the presence of reducant and oxidant functions in the same molecule. The previous formulation as tin(II) nitrate oxide is revised to that above.
See other REDOX COMPOUNDS
See related METAL NITRATES

4521. Ammonium azide
[12164-94-2] **H_4N_4**

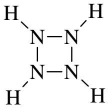


1. Mellor, 1940, Vol. 8, 344
2. Sorbe, 1968, 129
3. Obenland, C. O. *et al., Inorg. Synth.*, 1966, **8**, 53

It explodes on rapid heating [1] and contains ~93% of nitrogen. It is also friction- and impact-sensitive [2], and preparative precautions have been detailed [3].
See other HIGH-NITROGEN COMPOUNDS, NON-METAL AZIDES

4522. Tetraimide (Tetraazetidine)

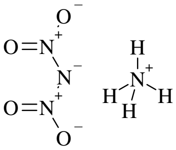
[58674-00-3] **H_4N_4**



Rice, F. O. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 1880—1881
This blue solid (a cyclic dimer of diazene, 93.3% of nitrogen), obtained by freezing out at —195°C the pyrolysis products of hydrogen azide, is extremely explosive above this temperature. An explosion at —125°C destroyed the apparatus.
See other HIGH-NITROGEN COMPOUNDS

4523a. Ammonium dinitramide

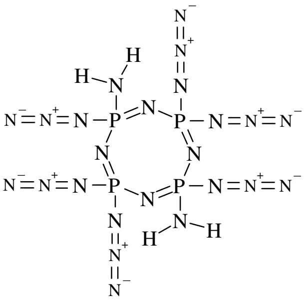
[140456-78-6] **$H_4N_4O_4$**



See Dinitramine
See other N—NITRO COMPOUNDS

4523b. 1,5-Diamino-1,3,3,5,7,7-hexaazidocyclotetraphosphazene (2,6-Diamino-2,4,4,6,8,8-hexaazido-2,2,4,4,6,6,8,8,-octahydro-1,3,5,7,2,4,6,8-tetraazotetraphosphosphocine)

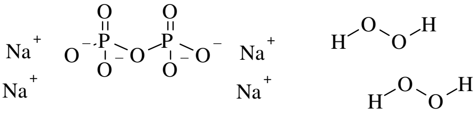
[332077-56-2] **$H_4N_{24}P_4$**



Forohar, F. *et al.*, US Pat. 6,218,554; *Chem. Abs.*, 2001, **134**, 2368411n
Claimed as representing of a new group of environmentally friendly explosives, the highly impact- and friction-sensitive oil sounds distinctly user-unfriendly.
See also ENVIRONMENTALISM
See other NON-METAL AZIDES

4524. Sodium perpyrophosphate

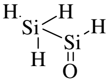
[18178-05-7] **$H_4Na_4O_{11}P_2$**



See Sodium pyrophosphate hydrogen peroxidate

4525. Oxodisilane

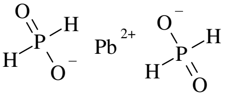
[22755-00-6] **H_4OSi_2**



Kautsky, K., *Z. Anorg. Chem.*, 1921, **117**, 209
It ignites in air.
See related SILANES

4526. Lead(II) phosphinate

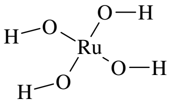
[10294-58-3] **$H_4O_4P_2Pb$**



Mellor, 1971, Vol. 8, Suppl. 3, 623
Impact-sensitive, used as priming explosive.
See other HEAVY METAL DERIVATIVES, METAL PHOSPHINATES, REDUCANTS

4527. Ruthenium(IV) hydroxide

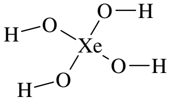
[12181-34-9] **H_4O_4Ru**



Mellor, 1942, Vol. 15, 516
It deflagrates incandescently above 300°C.

4528. Xenon(IV) hydroxide

[ ] **H_4O_4Xe**



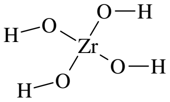
Sorbe, 1968, 158

Very unstable, it explodes violently on heating.

See other NON-METAL OXIDES, XENON COMPOUNDS

4529. Zirconium hydroxide

[14475-63-9] **H_4O_4Zr**

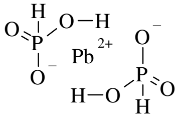


Zirconium

See Zirconium: Oxygen-containing compounds

4530. Lead(II) phosphite

[15521-60-5] **$H_4O_6P_2Pb$**



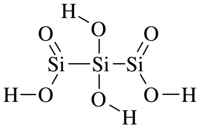
491M, 1975, 228

A fibre drum of the salt ignited spontaneously. This was attributed to slow decomposition with formation of phosphine which accumulated and eventually ignited inside the drum.

See other HEAVY METAL DERIVATIVES, REDUCANTS

4531. Tetrahydroxydioxotrisilane

[ ] **$H_4O_6Si_3$**



1. Mellor, 1940, Vol. 6, 230
2. Müller, R. *et al., J. Prakt. Chem.*, 1966, **31**, 1—6

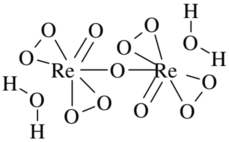
The hydrolysis product of octachlorotrisilane (and probably polymeric), it decomposes violently or explosively when heated in air, or sometimes spontaneously [1], and ignites when subjected to friction [2].

See Poly(dihydroxydioxodisilane)

See related NON-METAL OXIDES

4532. Oxobis[aqua(oxo)diperoxorheniumVII]

[174753-06-1] **$H_4O_{13}Re_2$**



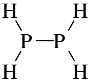
Herrmann, W. A. *et al., Chem. Eur. J.*, 1996, **2**(2), 168

An explosive red/orange solid, obtained from dirhenium heptoxide and hydrogen peroxide reacting in ether as solvent.

See other INORGANIC PEROXIDES

†4533. Diphosphane

[13445-50-6] **H_4P_2**



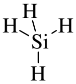
Mellor, 1940, Vol. 8, 829

It ignites in air, and will cause other flammable gases to ignite when present at 0.2 vol% concentration.

See other PHOSPHINES

†4534. Silane

[7803-62-5] **H_4Si**



1. Mellor, 1940, Vol. 6, 220—221
2. Braker, 1980, 632
3. Gale, H. J., *Lab. Haz. Bull.*, 1984, (3), item 140
4. Britton, L. G., *Plant/Oper. Progr.*, 1990, **9**(1), 16
5. Katou, Y., *Chem. Abs.*, 1990, **113**, 84061h
6. Kondo, S. *et al., Combust. Flame*, 1994, **97**(3-4), 296.
7. Horiguchi, S., *Chem. Abs.*, 1997, **127**, 143180k; *ibid.*, 1999, **130**, 104342g
8. Tsang, W. *et al, Chem. Abs.*, 2000, **132**, 139362g
9. Tamanini, F. *et al., Process Safety Progr.*, 1998, **17**(4), 243
10. Hirano, T. J., *J. Loss Prevent. Process Ind.*, 2004, **17**(1), 29

It is mildly endothermic (ΔH_f° (g) +32.5 kJ/mol, 1.01 kJ/g). Pure material is said not to ignite in air unless the temperature be increased or the pressure reduced. Presence of other hydrides as impurities causes ignition always to occur on contact [1]. However, 99.95% pure material, even at concentrations down to 1% in hydrogen and/or nitrogen, ignites in contact with air unless emerging at very high gas velocity, when mixtures with up to 10% silane content may not ignite [2]. Silane from a cylinder at 24 bar contained inside a ventilated cabinet inadvertently flowed back to the low pressure side of a nitrogen cylinder regulator outside the cabinet. When the regulator failed, the leaking silane ignited and burned outside the cabinet, preventing access to the main silane valve, and the leak reignited after extinguishing the fire. The system has been redesigned to eliminate the problems [3]. An exhaustive review of combustion and associated hazards is found in [4]. This also reveals potentially dangerous deflagration with the chlorofluoromethanes used in some fire extinguishers. A detailed study of silane flammability and blast effects in mixtures with nitrogen discharged to air [5]. The lower flammable limit of silane in air declines with decreasing oxygen content [6]. A Japanese review of explosion hazards with silane has been published. Spontaneous combustion in (somewhat oxygen depleted) air has been observed down to —162°C. In addition to the materials listed separately below, trifluoramine, interhalogens and a range of fluorocarbons and halofluorocarbons form explosive mixtures, as do sulfur tetra- and hexa-fluorides. Most of these are described as pyrophoric with silane, which may be a mistranslation [7]. It is claimed that trace quantities (a few hundred ppm) of iodine or hydrogen iodide render silane non-pyrophoric. It is not clear from the abstract whether hard science supplemented computer modelling in reaching this conclusion [8]. A study of explosivity in air showed autoignition above 4%, after a delay of up to two minutes shortening as silane concentration increased. Ventilation requirements for enclosed spaces into which leaks might occur were defined [9]. Extensive use of silane in the electronics industry has caused major accidents from uncontrolled mixing with air, Japanese experience is reviewed [10].

See also Oxygen, below

See other IGNITION SOURCES

Air, *cis*-2-Butene

Urtiew, P. A. *et al., Rept. UCRL-52007*, Richmond (Va.), USNTIS, 1976

Presence of the alkene delays or prevents spontaneous ignition of silane—air mixtures.

Halogens, or Covalent chlorides MRH values below references

1. Mellor, 1940, Vol. 6, 220—221
2. Braker, 1980, 632

MRH Bromine 1.21/91, carbon tetrachloride 2.89/83, chlorine 3.85/82

Silane burns in contact with bromine, chlorine or covalent chlorides (carbonyl chloride, antimony pentachloride, tin(IV) chloride, etc.) [1]. Extreme caution is necessary when handling silane in systems with halogenated compounds, as a trace of free halogen may cause violent explosions [2].

Nitrogen oxides

Horiguchi, S. *et al., Chem. Abs.*, 1990, **112**, 121711

Mixtures of silane and nitrogen oxides have been studied, that with nitrous oxide detonates very easily.

Other reactants

Yoshida, 1980, 371

MRH values calculated for 4 combinations with the materials indicated are given.

Oxygen MRH 14.31/66

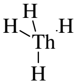
1. Bailar, 1973, Vol. 1, 1366
2. Ring, M. A. *et al., AIP Conf. Proc.*, 1988, **166** (Photovolt. Safety), 175—182

Very pure silane does not immediately explode with oxygen, but the decomposition products may ignite after a delay [1]. Mixtures of silane with 30% oxygen are metastable and potentially explosive under all pressure conditions studied, and become explosive at above 80°C. Addition of a few % of disilane renders the mixtures much more explosive, and mechanisms are proposed [2].

See other SILANES

4535. Thorium hydride

[15457-87-1] **H_4Th**



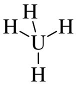
1. Mellor, 1941, Vol. 7, 207
2. Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64
3. Hartmann, I. *et al., Rept. Invest. No. 4835*, Washington, US Bur. Mines, 1951

Thorium hydride explodes on heating in air [1], and the powdered hydride readily ignites on handling in air [2]. Layers of thorium or uranium hydrides ignited spontaneously after exposure to ambient air for a few min [3].

See other METAL HYDRIDES

4536. Uranium(IV) hydride

[51680-55-8] **H_4U**



1. Hartmann, I. *et al., Rept. Invest. No. 4835*, Washington, US Bur. Mines, 1951
2. Starks, D. F. *et al., J. Amer. Chem. Soc.*, 1973, **95**, 3423

Layers of uranium or thorium hydrides ignited spontaneously after exposure to ambient air for a few min [1]. Thermal decomposition yields pyrophoric uranium [2].

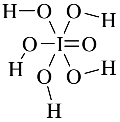
Oxygen

See Oxygen (Gas): Metal hydrides

See other METAL HYDRIDES

4537. Orthoperiodic acid

[10450-60-9] **H_5IO_6**



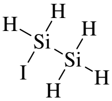
Azo-pigment, Perchloric acid

See Perchloric acid: Azo-pigment, etc.

See other INORGANIC ACIDS, OXOHALOGEN ACIDS

4538. Iododisilane

[14380-76-8] **H_5ISi_2**



Bailar, 1973, Vol. 1, 1371

It ignites in air.

See other HALOSILANES, IODINE COMPOUNDS

4539. Ammonium hydroxide

[1336-21-6] **H_5NO**

(*MCA SD-13*, 1947); *NSC 701*, 1983; *HCS 1980*, 140

Nitromethane

See Nitromethane: Acids, etc.

Other reactants

Yoshida, 1980, 211

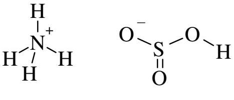
MRH values calculated for 11 combinations with oxidants are given.

See other INORGANIC BASES

See related NON-METAL HYDRIDES

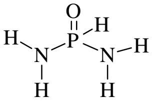
4540. Ammonium hydrogen sulfite

[10192-30-0] **H_5NO_3S**



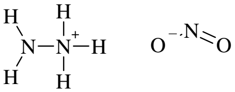
Self accelerating decomposition (Q = 0.43 kJ/g) occurs at 130°C in closed systems, such as are used for the Bucherer reaction.
See entry SELF-ACCELERATING REACTIONS

4542. Diamidophosphorous acid
[22750-67-0] **H_5N_2OP**



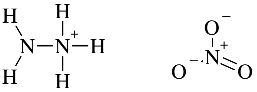
Water
Mellor, 1940, Vol. 8, 704
Interaction is violent with incandescence.
See other INORGANIC ACIDS

4543. Hydrazinium nitrite
[ ] **$H_5N_3O_2$**



See entry NITRITE SALTS OF NITROGENOUS BASES

4544. Hydrazinium nitrate
[13464-97-6] **$H_5N_3O_3$**



Alone, or Metals, or Metal compounds
Mellor, 1940, Vol. 8, 327; 1967, Vol. 8, Suppl. 2.2, 84, 96
It is an explosive of positive oxygen balance, less stable than ammonium nitrate, and has been studied in detail. Stable on slow heating to 300°C, it decomposes explosively on rapid heating or under confinement. Presence of zinc, copper, most other metals and their acetylides, nitrides, oxides or sulfides cause flaming decomposition above the m.p. (70°C). Commercial cobalt (cubes) causes an explosion also.

2-Hydroxyethylamine
Fujihara, S. *et al., Chem. Abs.*, 1976, **84**, 7212
Mixtures of the salt (80%) and amine (15%) with water are useful as an impact-insensitive but powerful liquid explosive.

Potassium dichromate

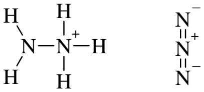
Shidlovskii, A. A. *et al., Chem. Abs.*, 1960, **54**, 22132g

Thermal decomposition becomes explosive above 270°C, or above 100°C in presence of 5% of potassium dichromate.

See other OXOSALTS OF NITROGENOUS BASES, REDOX COMPOUNDS

4545. Hydrazinium azide

[38551-29-0] **H_5N_5**

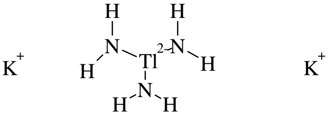


It contains some 94% of nitrogen.

See other HIGH-NITROGEN COMPOUNDS, HYDRAZINIUM SALTS, NON-METAL AZIDES

4546. Potassium triamidothallate ammoniate

[ ] **$H_6K_2N_3Tl.xNH_3$**



Alone, or Acids, or Water

Mellor, 1940, Vol. 8, 262

Like thallium(I) amide from which it is derived by treatment with potassium amide in liquid ammonia, the ammoniated salt (x = 2 or less) explodes violently on heating, friction, or contact with dilute acids or water.

See other N-METAL DERIVATIVES

4547. Lanthanum pentanickel hexahydride

[54847-21-1] **H_6LaNi_5**

$LaNi_5H_6$

Imamoto, T. *et al., J. Org. Chem.*, 1987, **52**, 5695—5699

The alloy hydride has been investigated as a useful hydrogenation catalyst for a wide variety of substrates under mild conditions. It is however pyrophoric in air, and an experimental procedure has been developed to avoid this hazard. A related hydride, $LaNi_{4.5}Al_{0.5}H_5$ has similar properties.

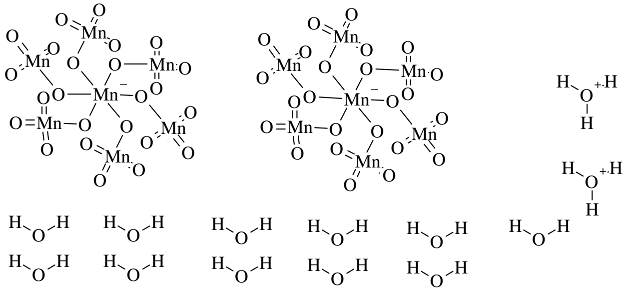
See Lanthanum—nickel alloy

See LANTHANIDE—TRANSITION METAL ALLOY HYDRIDES

4548. Dioxonium hexamanganato(VII)manganate

[51184-04-4]

[54065-28-0] (new unsolv. structure $H_2Mn_7O_{24}$) **$H_6Mn_{14}O_{52}.11H_2O$**



Krebs, B. *et al., Angew. Chem. (Intern. Ed.)*, 1974, **13**, 603

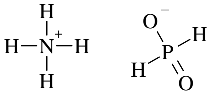
It has been shown that ‘solid permanganic acid dihydrate’, the powerful and unstable oxidant, is an undecahydrate as formulated above.

See Permanganic acid

See other INORGANIC ACIDS, OXIDANTS

4549. Ammonium phosphinate

[7803-65-8] **H_6NO_2P**



Mellor, 1940, Vol. 8, 880

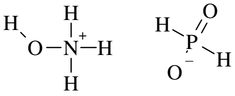
The salt evolves spontaneously flammable phosphine around 240°C.

See other REDUCANTS

See related METAL PHOSPHINATES

4550. Hydroxylaminium phosphinate

[ ] **H_6NO_3P**



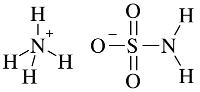
Mellor, 1940, Vol. 8, 880

The salt detonates above its m.p., 92°C.

See other HYDROXYLAMINIUM SALTS, REDUCANTS

See related METAL PHOSPHINATES

4551. Ammonium amidosulfate (Ammonium sulfamate)
[7773-06-0] **$H_6N_2O_3S$**

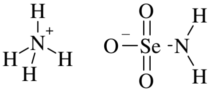


1. Hunt, J. K., *Chem. Eng. News*, 1952, **30**, 707
2. Rogers, M. G., private comm., 1973

A 60% solution of ammonium sulfamate (pH above 4.5) will not undergo rapid hydrolysis below 200°C. Addition of acid (to pH 2) causes a runaway exothermic hydrolysis to set in at 130°C. Superheating and vigorous boiling can occur under appropriate physical conditions [1]. The use of urea—formaldehyde resins as temporary binders in the firing of refractories and ceramics at high temperatures can lead to the formation of substantial deposits of ammonium sulfamate in the cooler parts of kilns, should a fuel oil containing appreciable amounts of sulfur be used for firing. Ammonia from decomposition of the resin combines with sulfur trioxide to form ammonium sulfamate which accumulates as either a solidified deposit in flues or as a white deposit on walls, causing corrosion and handling problems [2].

See other CORROSION INCIDENTS, OXOSALTS OF NITROGENOUS BASES, N—S COMPOUNDS

4552. Ammonium amidoselenate
[13767-10-7] **$H_6N_2O_3Se$**



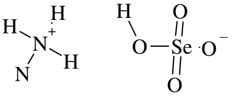
Dostal, K. *et al., Z. Anorg. Chem.*, 1958, **296**, 29—35

It explodes if rapidly heated to 120°C.

See other OXOSALTS OF NITROGENOUS BASES

See related N—S COMPOUNDS

4553. Hydrazinium hydrogen selenate
[ ] **$H_6N_2O_4Se$**



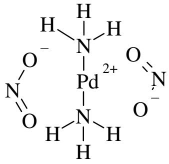
Meyer, J. *et al., Ber.*, 1928, **61**, 1839

The salt explodes in contact with a hot glass rod.

See other OXOSALTS OF NITROGENOUS BASES

4554. Diamminepalladium(II) nitrite

[28068-05-5] **$H_6N_4O_4Pd$**



Fountain, N. O., private comm., 1983

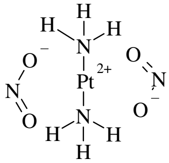
The dry salt is not readily ignitable, but is marginally more sensitive to impact than dinitrobenzene and can be ignited by impacted friction. The deflagration rate, once confined ignition had begun, was just greater than that of typical deflagrating explosives.

See other AMMINEMETAL OXOSALTS

See related PLATINUM COMPOUNDS

4555. *cis*-Diammineplatinum(II) nitrite

[14286-02-3] **$H_6N_4O_4Pt$**



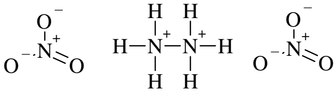
1. Brauer, 1965, Vol. 2, 1560
2. Holifield, P. J., private comm., 1974
3. Fountain, N. O., private comm., 1983

It decomposes explosively at 200°C [1]. Dry material stored in clear bottles in sunlight for several weeks became sensitive and exploded violently on slight mechanical shock. The material is now supplied commercially moistened with water [2]. The dry salt may be readily ignited, and deflagration under confinement is similar to that of gunpowder. Presence of 10% of water reduced ignitability but did not slow the deflagration rate thereafter. Sensitivity to impact or friction was greater than that of nitrobenzene [3].

See other AMMINEMETAL OXOSALTS, PLATINUM COMPOUNDS

4556. Hydrazinium dinitrate

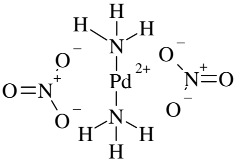
[13464-98-7] **$H_6N_4O_6$**



Sorbe, 1968, 130

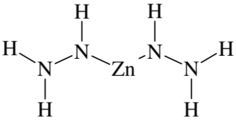
Like the mono-salt, it explodes on heating or impact.
See other OXOSALTS OF NITROGENOUS BASES

4557. Diamminepalladium(II) nitrate
[34090-17-0] **$H_6N_4O_6Pd$**



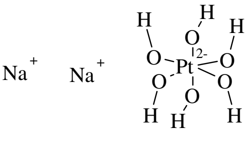
White, J. H., private comm., 1965
There is a danger of explosion if the nitrate is dried.
See other AMMINEMETAL OXOSALTS
See related PLATINUM COMPOUNDS

4558. Zinc dihydrazide
[25546-98-9] **H_6N_4Zn**



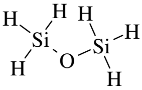
Mellor, 1940, Vol. 8, 315
It explodes at 70°C.
See other METAL HYDRAZIDES

4559. Sodium hexahydroxyplatinate(IV)
[12325-31-4] **$H_6Na_2O_6Pt$**



Acetic acid, Nitric acid
See Nitric acid: Acetic acid, Sodium hexahydroyxyplatinate(IV)
See other PLATINUM COMPOUNDS

4560. Disilyl oxide
[13597-73-4] **H_6OSi_2**



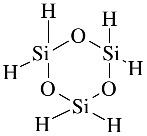
Chlorine

See Chlorine: Disilyl oxide

See related SILANES

4561. 2,4,6-Trisilatrioxane (Cyclotrisiloxane)

[291-50-9] **$H_6O_3Si_3$**



Air, or Chlorine

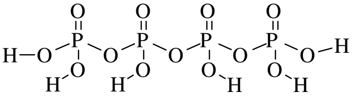
Mellor, 1940, Vol. 6, 234

The solid polymer (approximating to the trimer) ignites in air or chlorine.

See related SILANES

4562. Tetraphosphoric acid

[13813-62-2] **$H_6O_{13}P_4$**



Water

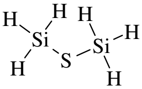
Mellor, 1971, Vol. 8, Suppl. 3, 736

Dilution of polyphosphoric acids with water in absence of cooling may lead to a large exotherm. Thus, tetraphosphoric acid diluted from 84 to 54% phosphorus pentoxide content rapidly attains a temperature of 120—140°C.

See other INORGANIC ACIDS

4563. Disilyl sulfide

[16544-95-9] **H_6SSi_2**



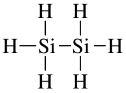
Sorbe, 1968, 127

It ignites in moist air.

See related NON-METAL SULFIDES, SILANES

†4564. Disilane

[1590-87-0] **H_6Si_2**



Bromine

See Bromine: Non-metal hydrides

Non-metal halides, or Oxygen

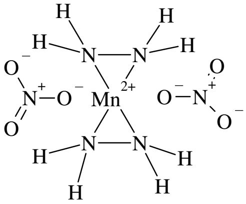
Mellor, 1940, Vol. 6, 220—224

It explodes on contact with carbon tetrachloride or sulfur hexafluoride, and contact with chloroform causes incandescence. Disilane ignites spontaneously in air, even when pure, and ingress of air or oxygen into a volume of disilane causes explosion.

See other SILANES

4565. Dihydrazinemanganese(II) nitrate

[39957-12-5] **$H_8MnN_6O_6$**



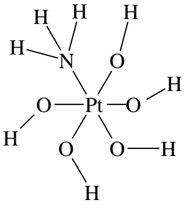
Bailar, 1973, Vol. 3, 827

It ignites at 150°C, but is not shock-sensitive.

See other AMMINEMETAL NITRATES

4566. Amminepentahydroxyplatinum

[ ] **H_8NO_5Pt**



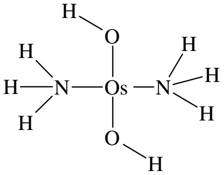
Jacobsen, J., *Compt. rend.*, 1909, **149**, 575

It explodes fairly violently above 250°C, as does the pyridine analogue.

See other N-METAL DERIVATIVES, PLATINUM COMPOUNDS

4567. Diamminedihydroxyosmium

[ ] **$H_8N_2O_2Os$**



Ephraim, 1939, 463

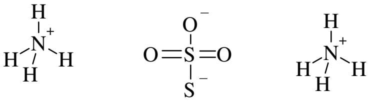
It decomposes vigorously on heating.

See other N-METAL DERIVATIVES

See related PLATINUM COMPOUNDS

4568. Ammonium thiosulfate

[7783-18-8] **$H_8N_2O_3S_2$**



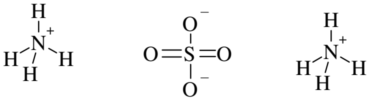
Sodium chlorate

See Sodium chlorate: Ammonium salts, etc.

See related N—S COMPOUNDS

4569. Ammonium sulfate

[7783-20-2] **$H_8N_2O_4S$**



Ammonium nitrate

See Ammonium Nitrate

Other reactants

Yoshida, 1980, 394

MRH values calculated for 14 combinations with various materials are given.

Potassium chlorate

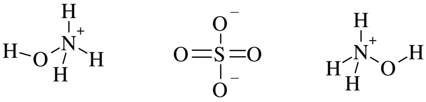
See Potassium chlorate: Ammonia, etc.

Sodium hypochlorite

See Sodium hypochlorite: Ammonium salts

See related METAL OXONON-METALLATES

4570. Hydroxylaminium sulfate
[10039-54-0] **$H_8N_2O_6S$**



FPA H66, 1978; *HCS 1980*, 559

1. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

The solid deflagrates at 5.6 cm/min, and will attain a maximum of 250 bar pressure in a closed system [1]. Energy of decomposition (in range 180—280°C) measured as 1.6 kJ/g [2].

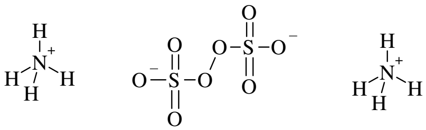
See other DEFLAGRATION INCIDENTS

Aniline, Chloral hydrate

See 2,2,2-Trichloro-1,1-ethanediol

See entry HYDROXYLAMINIUM SALTS

4571. Ammonium peroxodisulfate (Ammonium persulphate)
[7727-54-0] **$H_8N_2O_8S_2$**



HCS 1980, 149

Energy of decomposition (in range 140—210°C) measured as 0.323 kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Aluminium, Water MRH Aluminium 5.90/24

Pieters, 1957, 30

A mixture including the powdered metal may explode.

Ammonia, Silver salts

Mellor, 1947, Vol. 10, 466

In conc. solutions the silver catalysed oxidation of ammonia to nitrogen may be very violent.

Azoisobutyronitrile

1. Anon., *Chemical Engineer*, 1993, **536**, 4
2. *The Fire at Allied Colloids Ltd.*, HSE Books, Sudbury UK, 1994

The azonitrile (AZDN) and ammonium persulphate were stored together as polymerisation initiators. The AZDN was warmed by a supposedly blanked-off steam pipe and partially decomposed, rupturing its kegs and falling onto the persulphate in sacks below. Some degree of mixing was effected by a falling keg lid piercing a sack and carrying the AZDN with it. Subsequent ignition of the explosive mix (exactly how is uncertain) caused explosion and a major fire. Though they serve the same purpose, oxidants should not be stored with reducants.

See Azoisobutyronitrile

See RADICAL INITIATORS

Iron MRH 0.92/22

Mellor, 1947, Vol. 10, 470

Iron exposed to the action of a slightly acid conc. solution of ammonium peroxodisulfate dissolves violently.

Other reactants

Yoshida, 1980, 328

MRH values calculated for 11 combinations, largely with oxidisable materials, are given.

Sodium peroxide MRH 2.72/40

See Sodium peroxide: Ammonium peroxodisulfate

Sodium sulphide

Zhang, G-S. *et al., Loss Prevention and Safety Promotion in the Process Industries*, Vol I, (Mewis, J. J., Pasman, H. J. & De Rademaker, E. E. Eds.), 277, Amsterdam, Elsevier, 1995

An account of a serious warehouse explosion (15 dead, 141 injured). The two principal detonations were mostly due to ammonium nitrate, of which some hundred tonnes had been present, but the initiating fire was first observed in ammonium persulfate. This had been promiscuously stored alongside potassium permanganate, matches, potassium nitrate and sodium sulphide (or possibly sulphite), inter alia. None of these would improve the safety of ammonium persulfate. It was shown that the persulphate gives an immediate exothermic reaction with the sulphide. This was ascribed as the ultimate initiation. It was concluded that oxidants and reducants should not be mixed in storage [many other oxidants, such as permanganates, should not be trusted near a peroxy compound – Ed.] and that storage areas should be better separated one from another.

See also Potassium permanganate: Ammonium nitrate

Sulfuric acid

See CLEANING BATHS FOR GLASSWARE

Zinc, Ammonia

Rept. HM Insp. Explos., 33, London, HMSO, 1950

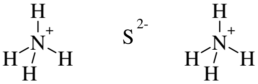
The salt exploded during drying, but no cause was determined. However, the reputed explosive character of tetraamminezinc peroxodisulfate, possibly formed from interaction of the ammonium salt, galvanised iron and ammonia, was mentioned as a possible cause.

See Tetraamminezinc peroxodisulfate

See other OXIDANTS, PEROXOACID SALTS

4572. Ammonium sulfide

[12135-76-1] : poly- (tri)sulfide is [12259-92-6] **H_8N_2S**



Zinc

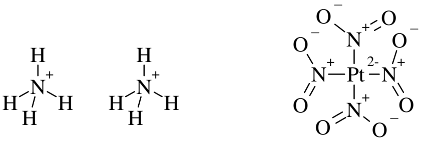
Anon., *Sichere Chemiearb.*, 1960, **12**(4), 29

A closed zinc container filled with a conc. solution of ammonium sulfide exploded, owing to liberation of hydrogen sulfide and hydrogen, accompanying the formation of zinc ammonium sulfide.

See related METAL SULFIDES

4573. Ammonium tetranitroplatinate(II)

[22289-82-3] (ion) **$H_8N_6O_8Pt$**



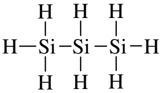
Nilson, L. F., *J. Prakt. Chem. [2]*, 1877, **16**, 249

It decomposes explosively on heating.

See other OXOSALTS OF NITROGENOUS BASES, PLATINUM COMPOUNDS

†4574. Trisilane

[7783-26-8] **H_8Si_3**



Air, or Carbon tetrachloride, or Oxygen

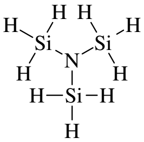
Mellor, 1940, Vol. 6, 224

It ignites and explodes in air or oxygen, and reacts vigorously with carbon tetrachloride.

See other SILANES

4575. Trisilylamine

[13862-16-3] **H_9NSi_3**



Air, or Ammonia, or Hydrogen

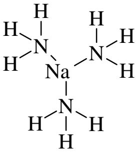
Mellor, 1940, Vol. 8, 262

The liquid ignites in air, and reacts vigorously with ammonia, hydrogen or moisture.

See related SILANES

4576. Sodium triammine

[84937-00-8] **H_9N_3Na**



Winter, R. *et al., Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 1093—1097

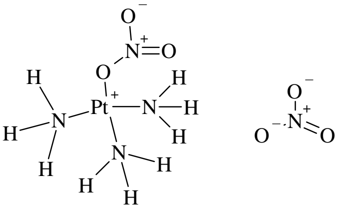
The new crystalline solid, metastable in liquid nitrogen, dissociates at ambient temperature and caused several sample tubes to explode from internal pressure of ammonia.

See other GAS EVOLUTION INCIDENTS

See related N-METAL DERIVATIVES

4577. Triamminenitratoplatinum(II) nitrate

[17524-18-4] **$H_9N_5O_6Pt$**



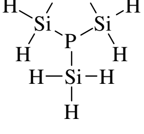
Mellor, 1942, Vol. 16, 409

It decomposes violently on heating.

See other AMMINEMETAL OXOSALTS, PLATINUM COMPOUNDS

4578. Trisilylphosphine

[15110-33-5] **H_9PSi_3**



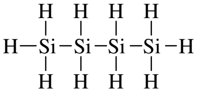
Amberger, E. *et al., Angew. Chem.*, 1962, **74**, 32—33

The liquid ignites in air.

See related PHOSPHINES, SILANES

4579. Tetrasilane

[7783-29-1] **$H_{10}Si_4$**



Air, or Carbon tetrachloride, or Oxygen

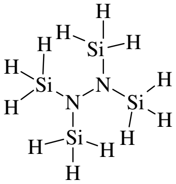
Mellor, 1940, Vol. 6, 224

It ignites and explodes in air or oxygen, and reacts vigorously with carbon tetrachloride.

See other SILANES

4580. Tetrasilylhydrazine

[25573-59-5] **$H_{12}N_2Si_4$**



Bailar, 1973, Vol. 1, 1377

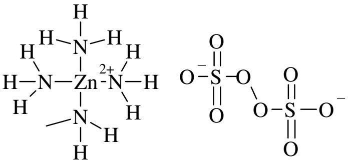
It explodes in air.

See SILYLHYDRAZINES

See related SILANES

4581. Tetraamminezinc peroxodisulfate

[39733-13-6] **$H_{12}N_4O_8S_2Zn$**



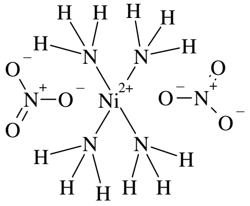
Barbieri, G. A. *et al., Z. Anorg. Chem.*, 1911, **71**, 347

It explodes on heating or impact.

See other AMMINEMETAL OXOSALTS

4582. Tetraamminenickel(II) nitrate

[15651-35-1] **$H_{12}N_6NiO_6$**

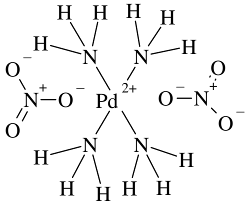


Explosive.

See other AMMINEMETAL NITRATES

4583. Tetraamminepalladium(II) nitrate

[13601-08-6] **$H_{12}N_6O_6Pd$**



White, J. H., private comm., 1965

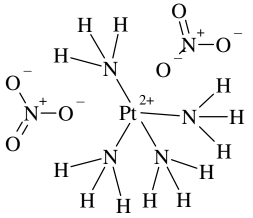
Evaporation of a solution of the salt used for plating gave a moist residue which ignited and burned violently. Reclamation of palladium from such solutions by direct reduction is recommended. It was subsequently shown to be explosive

See other AMMINEMETAL NITRATES

See related PLATINUM COMPOUNDS

4584. Tetraammineplatinum(II) nitrate (Tetraamminedinitratoplatinum)

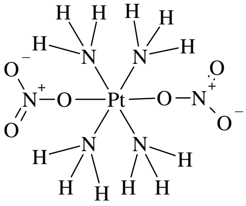
[20634-12-2] tetrahedral **$H_{12}N_6O_6Pt$**



Similar to the palladium complex (above)

See other AMMINEMETAL NITRATES, PLATINUM COMPOUNDS

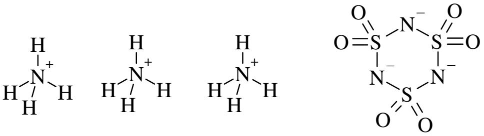
4585. Tetraammineplatinum(II) nitrate (Tetraamminedinitratoplatinum)
[133163-34-5] octahedral **$H_{12}N_6O_6Pt$**



Similar to the palladium complex (above)

See other AMMINEMETAL NITRATES, PLATINUM COMPOUNDS

4586. Ammonium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide (‘Ammonium triselenimidate’)
[ ] **$H_{12}N_6O_6Se_3$**

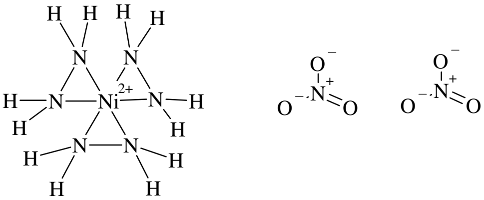


Explosive.

See Selenium difluoride dioxide: Ammonia

See related N—S COMPOUNDS

4587. Trihydrazinenickel(II) nitrate
[69101-54-8] **$H_{12}N_8NiO_6$**



Ellern, H. *et al., J. Chem. Educ.*, 1955, **32**, 24

A dry sample exploded violently and a moist sample spontaneouly deflagrated.

See other AMMINEMETAL NITRATES

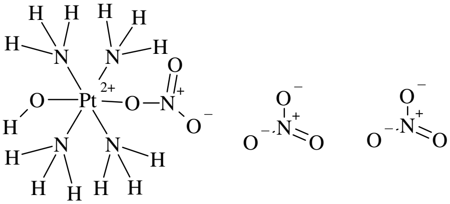
4588. Amminedecahydroxydiplatinum
[ ] **$H_{13}NO_{10}Pt$**

Unknown Structure

Jacobsen, J., *Compt. rend.*, 1909. **149**, 574—577

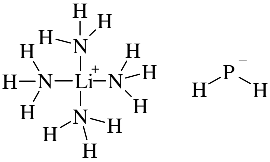
The compound, of unknown structure, explodes violently on heating.
See other PLATINUM COMPOUNDS

4589. Tetraamminehydroxynitratoplatinum(IV) nitrate
[ ] **$H_{13}N_7O_{10}Pt$**



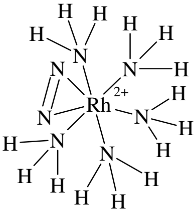
Mellor, 1942, Vol. 16, 411
It explodes violently on heating.
See other AMMINEMETAL OXOSALTS, PLATINUM COMPOUNDS

4590. Tetraamminelithium dihydrogenphosphide
[44023-01-6] **$H_{14}LiN_4P$**



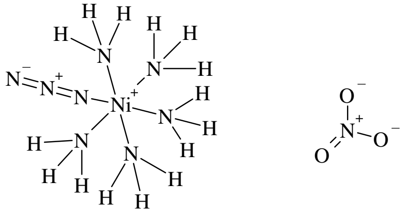
Water
Legoux, C., *Compt. rend.*, 1938, **207**, 634
It reacts vigorously with water, evolving phosphine and ammonia which may ignite.
See related METAL NON-METALLIDES

4591a. Pentaamminedinitrogenruthenium(II) salts
[19504-40-6] (ion) **$H_{15}N7Ru^{2+}$**



Preparative hazard
Hydrazine: Ruthenium(III) chloride
See Pentaamminechlororuthenium chloride: Sodium azide
See other N-METAL DERIVATIVES

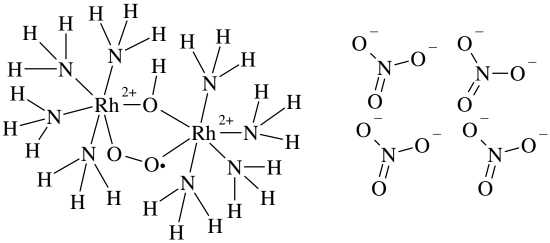
4591b. Azidopentamminenickel(1+) nitrate (Pentaammineazidonickel(1+) nitrate)
[234772-07-7] (ion) **$H_{15}N_9NiO_3$**



Photolytically explosive

See other AMMINEMETAL NITRATES

4592. Octaammine-*μ*-hydroxy[*μ*-superoxido-*O,O'*)]dirhodium(4+) nitrate
[113753-12-1] **$H_{25}N_{12}O_{15}Rh_2$**



Springborg, J. *et al., Acta Chem Scand. Sec. A*, 1987, **A41**, 485

The complex may detonate when subjected to mechanical shock.

See other AMMINEMETAL OXOSALTS

4593a. Undecaamminetetraruthenium dodecaoxide
[ ] **$H_{33}N_{11}O_{12}Ru_4$**

$[H_3N)_{11}Ru_4O_{12}]$

Preparative hazard

See Ruthenium(VIII) oxide: Ammonia

See related METAL OXIDES

4593b. Helium
[ ] **He**

He

Hempseed, J. W. *et al., Proc. 24th Ann. Loss Prev. Symp.*, 1990, 95c (Amer. Inst. Chem. Engineers)

Although helium is inert, it is not necessarily pure. An explosion during repurification of air-contaminated helium is reported. Purification was cryogenic and involved a carbon absorber. Liquid oxygen appears to have condensed in the top of the carbon bed, forming a Sprengel explosive, which duly exploded (safety problems were one

reason for abandoning the former use of this particular combination as an explosive). Liquid helium is the ultimate cryogen.
See other CRYOGENIC LIQUIDS

4594. Hafnium
[7440-58-6] **Hf**

Hf

Alone, or Non-metals, or Oxidants
(*MCA SD-52*, 1966)
Although the massive metal is relatively inert, when powdered it becomes very reactive. The dry powder may react explosively at elevated temperatures with nitrogen, phosphorus, oxygen, sulfur and other non-metals. The halogens react similarly, and in contact with hot conc. nitric acid and other oxidants it may explode (often after a delay with nitric acid). The powder is pyrophoric and readily ignitable by friction, heat or static sparks, and if dry burns fiercely. Presence of water (5—10%) slightly reduces the ease of ignition, but combustion of the damp powder proceeds explosively (the oxygen content of water, 89%, being much higher than that of air). A minimum of 25% water is necessary to reduce handling hazards to a minimum. Full handling precautions are detailed.
See other METALS, PYROPHORIC METALS

4595. Mercury
[7439-97-6] **Hg**

Hg

NSC 203, 1976; *HCS 1980*, 620; *RSC Lab. Hazards Data Sheet No. 47*, 1986

Acetylenic compounds
See 3-Bromopropyne: Metals MRH 2.18/99+
2-Butyne-1,4-diol: Alkalies, etc.
Sodium acetylide: Metals
See ACETYLENIC COMPOUNDS: Metals

Alkynes, Silver perchlorate
See Silver perchlorate: Alkynes, etc.

Ammonia
1. Sampey, J. J., *Chem. Eng. News.*, 1947, **25**, 2138
2. Braidech, M. M., *J. Chem. Educ.*, 1967, **44**, A324
3. Thodos, G., *Amer. Inst. Chem. Engrs. J.*, 1964, **10**, 274
4. Henderson, L. M., *Ind. Eng. Chem. (News Ed.)*, 1932, **10**, 73
5. Brunt, C. Van, *Science*, N.Y., 1927, **65**, 63—64

A mercury manometer used with ammonia became blocked by deposition of a grey-brown solid, which exploded during attempts to remove it mechanically or on heating. The solid appeared to be a dehydration product of Millon's base and was freely soluble in sodium thiosulfate solution. This method of cleaning is probably safer than others, but the use of mercury manometers with ammonia should be avoided as intrinsically

unsafe [1,2]. Although pure dry ammonia and mercury do not react even under pressure at 340 kbar and 200°C, the presence of traces of water leads to the formation of an explosive compound, which may explode during depressurisation of the system [3]. Explosions in mercury—ammonia systems had been reported previously [4,5].
See Poly(dimercuryimmonium hydroxide)
See also FULMINATING METALS
See other CORROSION INCIDENTS

Boron diiodophosphide
See Boron diiodophosphide: Metals

Ethylene oxide MRH 3.72/99+
See Ethylene oxide(reference 4)

Metals
Bretherick, L., *Lab. Pract.*, 1973, **22**, 533
The high mobility and tendency to dispersion exhibited by mercury, and the ease with which it forms alloys (amalgams) with many laboratory and electrical contact metals, can cause severe corrosion problems in laboratories. A filter—cyclone trap is described to contain completely mercury ejected accidentally by overpressuring of mercury manometers and similar items.
See Aluminium: Mercury
Calcium: Mercury
Lithium: Mercury
Potassium: Mercury
Rubidium: Mercury
Sodium: Mercury
See other CORROSION INCIDENTS

Methyl azide
See Methyl azide: Mercury

Methysilane, Oxygen
See Methylsilane: Mercury, etc.

Other reactants
Yoshida, 1980, 210
MRH values calculated for 6 combinations, largely with materials showing catalytic decomposition, are given.

Oxidants MRH 5.69/99+
See Bromine: Metals
Chlorine dioxide: Mercury
Chlorine: Metals (reference 1)
Nitric acid: Alcohols (reference 2)
Peroxyformic acid: Metals, etc.

Tetracarbonylnickel, Oxygen MRH Tetracarbonylnickel 0.88/99+
See Tetracarbonylnickel: Mercury, etc.
See other METALS

4596. Zinc amalgam

[72780-86-0] **Hg—Zn**

Hg—Zn

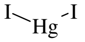
Brimelow, H. C., private comm., 1972

Amalgamated zinc residues isolated from Clemmensen reduction of an alkyl aryl ketone in glacial acetic acid were pyrophoric, and had to be immediately dumped into water after filtration to prevent ignition.

See other PYROPHORIC ALLOYS

4597. Mercury(II) iodide

[7774-29-0] **HgI_2**



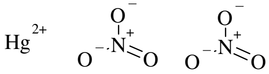
Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

See other MERCURY COMPOUNDS, METAL HALIDES

4598. Mercury(II) nitrate

[10045-94-0] **HgN_2O_6**



HCS 1980, 616

Acetylene

Mellor, 1940, Vol. 4, 993

Contact of acetylene with the nitrate solution gives mercury acetylide, an explosive sensitive to heat, friction or contact with sulfuric acid.

Ethanol

Mellor, 1940, Vol. 4, 993

Addition of mercury(II) nitrate solution to ethanol gives mercury fulminate.

Ferrocene

Sallott, G. P. *et al., Proc. Int. Pyrotech. Semin.*, 1984, 589—602

Compositions prepared from mercury(II) nitrate and ferrocene or its derivatives show promise as explosive priming mixtures, but such mixtures are fairly sensitive to electrostatic initiation and should be handled in the wet state.

Isobutene

See 2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane

Petroleum hydrocarbons

1. Mixer, R. Y., *Chem. Eng. News*, 1948, **26**, 2434
2. Ball, J., *Chem. Eng. News*, 1948, **26**, 3300

Gas oil was stirred vigorously with the finely divided solid nitrate to complete the removal of sulfur compounds. After the mixture had congealed, preventing further stirring, a violent reaction set in which reached incandescence, accompanied by vigorous evolution of nitrous fumes. This was attributed to the self-catalysed nitrating action of mercury nitrate in a semi-solid environment unable to lose heat effectively. A similar occurrence was observed when crushed nitrate was just covered with cracked naphtha [1]. The second publication reveals that this type of hazard was known in cracked distillates containing a high proportion of unsaturates and aromatics, when allowed to stand in prolonged contact with mercury(II) nitrate. The hazard may be avoided by using several small portions of the salt sequentially, and working with 100 g portions of hydrocarbons [2].

Phosphine
Mellor, 1940, Vol. 9, 993
Phosphine reacts with the aqueous salt solution to give a complex nitrate—phosphide, which when dry explodes on heating or impact.

Phosphinic acid
Mellor, 1940, Vol. 4, 993
Phosphinic (‘hypophosphorous’) acid violently reduces the salt to the metal.

Potassium cyanide
Rüst, 1948, 337
Mixtures exploded when heated, but only if contained in narrow ignition tubes. Formation of nitrite, a more powerful oxidant than nitrate, may have been involved.
See other MERCURY COMPOUNDS, METAL NITRATES, OXIDANTS

4599. Mercury(II) azide
[14215-33-9] **HgN_6**

$$N^{-}{=}N^{+}{=}N{-}Hg{-}N{=}N^{+}{=}N^{-}$$

1. Mellor, 1940, Vol. 8, 351; 1967, Vol. 8. Suppl. 2, 43, 50
2. Barton, A. F. M. *et al., Chem. Rev.*, 1973, **73**, 138
3. Heathcock, C. H., *Angew. Chem. (Intern. Ed.)*, 1969, **8**, 134

The very high friction-sensitivity, particularly of large crystals, and brisance on explosion are to be expected from the thermodynamic properties of the salt. Its great sensitivity, even under water, renders it unsuitable as a practical detonator [1]. Spontaneous explosions during intercrystalline transformations have been observed, or on crystallisation from hot water [2]. A safe method of preparing solutions in aqueous THF for synthetic purposes is available [3].

It is strongly endothermic (ΔH_f° (s) +556.5 kJ/mol, 1.96 kJ/g).
See other MERCURY COMPOUNDS, METAL AZIDES

4600. Mercury(II) oxide

[21908-53-2] **HgO**

$$Hg{=}O$$

HCS 1980, 617

Under appropriate conditions, it can function as a powerful oxidant and/or catalyst, owing to the tendency to dissociate to metal and oxygen.

Acetyl nitrate
See Acetyl nitrate: Mercury(II) oxide

Butadiene, Ethanol, Iodine
See 2-Ethoxy-1-iodo-3-butene

Chlorine
1. Tabata, Y. *et al., J. Haz. Mat.*, 1987, **17**, 55
2. Shilov, E. A., *Compt. Rend. Acad. Sci. USSR*, 1945, **46**, 64—65

Mercury(II) oxide reacts with chlorine to form dichlorine oxide which can explode at temperatures close to ambient [1]. This confirms a previous report [2].

Chlorine, Hydrocarbons
Methane: Halogens, etc.
Ethylene: Chlorine

Diboron tetrafluoride
See Diboron terafluoride: Metal oxides

Disulfur dichloride
See Disulfur dichloride: Mercury oxide

Hydrogen peroxide
See Hydrogen peroxide: Mercury(II) oxide, or: Metals, etc.

Hydrogen trisulfide
See Hydrogen trisulfide: Metal oxides

Metals
1. Staudinger, H., *Z. Elektrochem.*, 1925, **312**, 549
2. Mellor, 1940, Vol. 4, 272

Mixtures of the red or yellow oxides with sodium—potassium alloy explode violently on impact, the yellow (more finely particulate) oxide giving the more sensitive mixture [1]. Mixtures with magnesium or potassium may explode on heating [2].

Methanethiol
Klason, P., *Ber.*, 1887, **20**, 3410
Interaction is rather violent in absence of diluent.

Non-metals
Mellor, 1940, Vol. 4, 777—778

Mixtures with phosphorus explode on impact or on boiling with water. A mixture with sulfur explodes on heating.

Phospham

See Phospham: Oxidants

Reducants

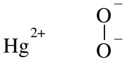
Mellor, 1940, Vol. 4, 778; Vol. 8, 318

Hydrazine hydrate and phosphinic acid both explosively reduce the oxide when dropped on to it.

See other MERCURY COMPOUNDS, METAL OXIDES, OXIDANTS

4601. Mercury peroxide

[12298-67-8] **HgO_2**



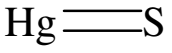
Preparative hazard

See Hydrogen peroxide: Mercury(II) oxide, etc.

See other MERCURY COMPOUNDS, METAL PEROXIDES

4602. Mercury(II) sulfide

[1344-48-5] **HgS**



Oxidants

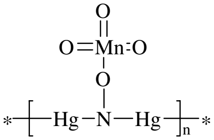
Mellor, 1941, Vol. 2, 242; 1941, Vol. 3, 377; 1940, Vol. 4, 952

The sulfide causes dichlorine oxide to explode, and it incandesces in chlorine. Grinding with silver oxide ignites the mixture.

See other MERCURY COMPOUNDS, METAL SULFIDES

4603. Poly(dimercuryimmonium permanganate)

[ ] **$(Hg_2MnNO_4)_n$**



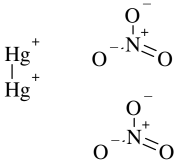
Sorbe, 1968, 97

It is highly explosive.

See other POLY(DIMERCURYIMMONIUM) COMPOUNDS

4604. Mercury(I) nitrate

[10415-75-5] **$Hg_2N_2O_6$**



Carbon

Mellor, 1940, Vol. 4, 987

Contact with red-hot carbon causes a mild explosion.

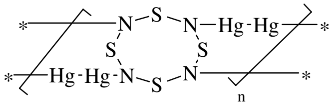
Phosphorus

See Phosphorus: Nitrates

See other MERCURY COMPOUNDS, METAL NITRATES

4605. Mercury(I) thionitrosylate

[ ] **$(Hg_2N_2S_2)_n$**



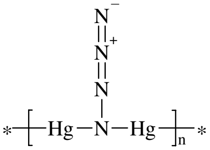
Goehring, M. *et al., Z. Anorg. Chem.*, 1956, **285**, 702

It explodes on heating in a flame. The structure may be the indicated linear polymer of tetrasulfur tetraimidate rings linked by pairs of dimercury bonds.

See other MERCURY COMPOUNDS, N—S COMPOUNDS

4606. Poly(dimercuryimmonium azide)

[ ] **$(Hg_2N_4)_n$**



Sorbe, 1968, 97

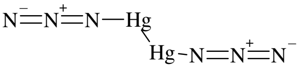
It is highly explosive.

See other POLY(DIMERCURYIMMONIUM) COMPOUNDS

See related METAL AZIDES

4607. Mercury(I) azide

[38232-63-2] **Hg_2N_6**



Mellor, 1940, Vol. 8, 351; 1967, Vol. 8, Suppl. 2, 25, 50

It is less sensitive and a less powerful explosive than silver azide or lead azide. It explodes on heating in air to above 270°C, or after an induction period at 140°C in the dark under vacuum.

See other INDUCTION PERIOD INCIDENTS, MERCURY COMPOUNDS, METAL AZIDES

4608. 'Mercury(I) oxide'

[15829-53-5] **Hg_2O**

$$Hg \qquad Hg^{2+} \qquad O^{2-}$$

Sidgwick, 1950, 292

The material is known to be an intimate mixture of mercury(II) oxide and finely dispersed metallic mercury.

Alkali metals

Mellor, 1940, Vol. 4, 771

Interaction with molten potassium or sodium is accompanied by a brilliant light and a light explosion.

Chlorine, Ethylene

See Ethylene: Chlorine

Hydrogen peroxide MRH 1.59/99+

Antropov, V., *J. Prakt. Chem.*, 1908, **77**, 316

Contact causes explosive decomposition of the peroxide.

See Hydrogen peroxide: Metals, etc.

Non-metals

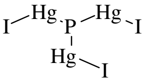
Mellor, 1940, Vol. 4, 771

Mixtures with phosphorus explode on impact, and that with sulfur ignites on frictional initiation.

See other MERCURY COMPOUNDS, METAL OXIDES

4609. Tris(iodomercurio)phosphine

[ ] **Hg_3I_3P**

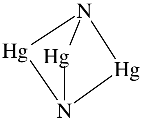


Nitric acid

See Nitric acid: Phosphine derivatives

See related MERCURY COMPOUNDS, PHOSPHINES

4610. Mercury nitride
[12136-15-1] **Hg_3N_2**



Alone, or Sulfuric acid.

1. Mellor, 1940, Vol. 8, 108
2. Fischer, F. *et al., Ber.*, 1910, **43**, 1469
3. Wilhelm, S. M., *Plant/Oper. Progr.*, 1991, **10**(4), 192

It explodes on friction, impact, heating or in contact with sulfuric acid [1]. A sample at below —40°C exploded when disturbed [2]. It may form from the metal and ammonia in some circumstances [3].

See other FULMINATING METALS, MERCURY COMPOUNDS, N-METAL DERIVATIVES

4611. Trimercury tetraphosphide
[12397-29-4] **Hg_3P_4**

Hg_3P_4

Oxidants

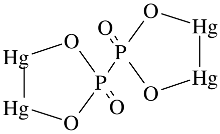
Mellor, 1940, Vol. 8, 844

It ignites when warmed in air, or cold on contact with chlorine. A mixture with potassium chlorate explodes on impact.

See Potassium chlorate: Metal phosphides

See other MERCURY COMPOUNDS, METAL NON-METALLIDES

4612. Mercury(I) hypophosphate
[ ] **$Hg_4O_6P_2$**



Mellor, 1971, Vol. 8, Suppl. 3, 651

Explosive decomposition occurs on heating.

See other MERCURY COMPOUNDS

4613. Potassium iodide
[7681-11-0] **IK**

K^+ I^-

HCS 1980, 770

Charcoal, Ozone

See Ozone: Charcoal, Potassium iodide

Diazonium salts

See DIAZONIUM TRIIODIDES

Diisopropyl peroxydicarbonate

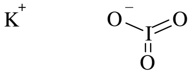
See Diisopropyl peroxydicarbonate (reference 2)

Oxidants

See Bromine pentafluoride: Acids, etc.
See Chlorine trifluoride: Metals, etc.
See Fluorine perchlorate: Alone, etc.
See Trifluoroacetyl hypofluorite
See other METAL HALIDES

4614. Potassium iodate

[7758-05-6] **IKO_3**



HCS 1980, 769

Charcoal, Ozone

See Ozone: Charcoal, Potassium iodide

Metals and oxidisable derivatives

Phosphorus: Metal halogenates
See other METAL HALOGENATES: Metals and oxidisable derivatives

Other reactants

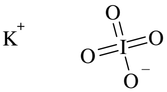
Yoshida, 1980, 376
MRH values calculated for 27 combinations with oxidisable materials are given.

Sodium disulfite, Water

Association for Science Education, Internet, 1997
A student, who should have mixed solutions of these two salts, mixed the solids and added water, which provoked a violent reaction. It is suggested that pupils should not be allowed access to solid, undiluted, oxidants and reductants at the same time.
See other IODINE COMPOUNDS, METAL HALOGENATES, OXIDANTS

4615. Potassium periodate

[7790-21-8] **IKO_4**



HCS 1980, 773

Ammonium perchlorate

See Ammonium perchlorate: Impurities

See other IODINE COMPOUNDS, METAL OXOHALOGENATES, OXIDANTS

4616. Iodine azide

[14696-82-3] **IN_3**

$$\overset{-}{N}=\overset{+}{N}=N-I$$

1. Hantzsch, A., *Ber.*, 1900, **33**, 525
2. Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1976, **15**, 553
3. Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1979, **18**, 507—514
4. Klapötke, T. M. *et al., Angew. Chem. (Int.)*, 1993, **32**(2), 275
5. Marinescu, L. G., *et al., Tetrahedron*, 2005, **61**(1), 123

The isolated solid is a very shock- and friction-sensitive explosive [1], but the preparation and safe handling of dilute solutions in solvents other than ether have been described [2]. The need to use appropriate techniques and precautions when using iodine azide as a reagent is stressed [3]. The purer the more explosive; explosive properties are characterised (lead-block test, etc.) in a footnote to [4]. A safe way of generating and using it as a polymer supported reagent is advanced [5].

Sulfur-containing alkenes

Hassner, A. *et al., J. Org. Chem.*, 1968, **33**, 2690

Interaction is accompanied by violent decomposition of the azide.

See other HALOGEN AZIDES

4617. Iodinated poly(sulfur nitride)

[ ] **$(IN_{4.2}S_6)_n$**

Unknown Structure

Banister, A. J. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 937

The polymeric product is potentially explosive.

See other IODINE COMPOUNDS, N—S COMPOUNDS

4618. Sodium iodide

[7681-82-5] **INa**

$$Na^{+} \qquad I^{-}$$

HCS 1980, 849

Oxidants

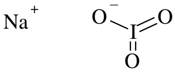
Perchloric acid: Iodides

See Perchloryl fluoride: Calcium acetylide, etc.

See other METAL HALIDES

4619. Sodium iodate

[7681-55-2] **$INaO_3$**



Metals MRH Magnesium 5.98/27

Webster, H. A. *et al., Rept. AD-782510/2GA*, Springfield (Va.), USNTIS, 1974

The use of mixtures with magnesium in pyrotechnic flares is discussed.

See Potassium: Oxidants MRH 1.42/31

Sodium: Iodates MRH 3.10/42

Other reactants

Yoshida, 1980, 381—382

MRH values calculated for 27 combinations with oxidisable materials are given.

See other IODINE COMPOUNDS, METAL HALOGENATES, OXIDANTS

4620. Iodine

[7553-56-2] **I_2**

I—I

(*MCA SD-43*, 1952); *NSC 457*, 1968; *HCS 1980*, 560

Acetaldehyde

MCA SD-43, 1952

Interaction may be violent.

Acetylene MRH 8.70/99+

See Acetylene: Halogens

Aluminium, Diethyl ether

Garcia, F. J. A., *Inorg. Chem.*, 1980, **20**, 83

In the preparation of aluminium iodide etherate from the elements in ether, the aluminium must be as turnings, rather than fine powder, to keep the reaction under control.

See Aluminium: Halogens

Ammonia

Mellor, 1940, Vol. 8, 605; 1967, Vol. 8, Suppl. 2.2, 416

Ammonia solutions react with iodine (or potassium iodide) to produce highly explosive addition compounds of nitrogen triiodide and ammonia.

See Nitrogen triiodide—ammonia

Ammonia, Lithium 1-heptynide

Houben-Weyl, 1977, Vol. 5.2a, 605

Reaction of iodine with the lithium heptynide in liquid ammonia to give (explosive) 1-iodoheptyne may lead to formation of nitrogen triiodide as a black precipitate. Low temperatures minimise the formation, and it may be destroyed by adding sodium ethoxide solution.

Ammonia, Potassium
See Ammonia: Iodine, Potassium

Butadiene, Ethanol, Mercuric oxide
See 2-Ethoxy-1-iodo-3-butene

Caesium oxide
See Caesium oxide: Halogens

Dipropylmercury
See Dipropylmercury: Iodine

Ethanol, Phosphorus
1. Read, C. W. W., *School Sci. Rev.*, 1940, **21**(83), 967
2. Llowarch, D., *School Sci. Rev.*, 1956, **37**(133), 434

Interaction of ethanol, phosphorus and iodine to form iodoethane was considered too dangerous for a school experiment [1]. A safer modification is now available [2].
See Phosphorus: Halogens

Formamide, Pyridine, Sulfur trioxide
See Formamide: Iodine, etc.

Halogens, or Interhalogens
See Bromine trifluoride: Halogens
Bromine pentafluoride: Acids, etc.
Chlorine trifluoride: Iodine
Fluorine: Halogens, etc.

Metal acetylides or carbides MRH values show % of those
Several react very exothermally with iodine.
See Barium acetylide: Halogens
Caesium acetylide: Halogens
Calcium acetylide: Halogens MRH 1.46/20
Dicopper(I) acetylide: Halogens
Lithium acetylide: Halogens
Rubidium acetylide: Halogens
Strontium acetylide: Halogens MRH 1.34/31
Zirconium dicarbide: Halogens

Metals MRH Lithium 2.01/5, potassium 1.97/24
1. Mellor, 1941, Vol. 2, 469; 1963, Vol. 2, Suppl. 2.2, 1563; 1939, Vol. 9, 379
2. Tarnqvist, E. G. M. *et al., Inorg. Chem.*, 1979, **18**, 1793

Iodine and antimony powder react so violently as to cause ignition or explosion of the bulk of the mixture. A mixture of potassium and iodine explodes weakly on impact, while potassium ignites in contact with molten iodine [1]. Interaction of molten iodine with titanium above 113°C under vacuum to form titanium tetraiodide is highly exothermic and sparks are produced. The preparative technique described permits the progressive reaction of 0.5 g portions of the titanium powder charged (7.2 g) to minimise hazard [2].

See Aluminium: Oxidants
Aluminium—titanium alloys: Oxidants
Hafnium: Alone, etc.
Sodium: Halogens (reference 5)

Metals, Water
Jackson, H., *Spectrum*, 1969, **7**, 82
Flash-ignition occurs when mixtures of iodine with powdered aluminium, magnesium or zinc are moistened with a drop of water.

Non-metals
See Boron: Halogens
Phosphorus: Halogens

Other reactants
Yoshida, 1980, 372
MRH values calculated for 8 combinations, largely with oxidisable materials, are given.

Oxygen difluoride
See Oxygen difluoride: Halogens, etc.

Poly(acetylene)
Pekker, S. *et al., Chem. Abs.*, 1983, **99**, 213009
In TGA studies on the decomposition of iodine-doped polyacetylene, at high heating rates (30°C/min), decomposition becomes explosive at the m.p. of iodine, 113°C. This was attributed to exothermic reaction of liquid iodine with polyacetylene.

Silver azide MRH 2.05/99+
See Silver azide: Halogens

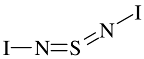
Sodium phosphinate
See Sodium phosphinate: Oxidants

Tetraamminecopper(II) sulfate, Ethanol
Schwarzenbach, V., *Ber.*, 1875, **8**, 1233
Addition of ethanol to a mixture of iodine and the salt soon led to explosions of variable intensity, involving formation of *N*-iodo derivatives.
See Mercury(II) amide chloride: Halogens

Trioxygen difluoride
See 'Trioxygen difluoride': Various materials
See other HALOGENS, OXIDANTS

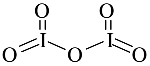
4621. *N,N′*-Diiodosulfurdiimide

[ ] **I_2N_2S**



Seppelt, K. *et al., Angew. Chem. (Int.)*, 1969, **8**, 771
This explodes both on melting and impact. The bromo-analogue is more sensitive, the chloro-compound is not known.
See other N-HALOGEN COMPOUNDS, IODINE COMPOUNDS, N—S COMPOUNDS

4622. Iodine(V) oxide
[12029-98-0] **I_2O_5**



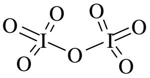
Aluminium
Ivanov, V. G. *et al., Chem. Abs.*, 1981, **95**, 9423
Combustion of compressed mixtures of metal powder and the oxide is very vigorous, a layer of molten aluminium being produced initially, followed by a jet of flame.

Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.

Hydrazine
See Hydrazine: Iodine pentoxide

Non-metals
Mellor, 1941, Vol. 2, 295
Iodine pentaoxide reacts explosively with warm carbon, sulfur, rosin, sugar or powdered, easily combustible elements
See other HALOGEN OXIDES, IODINE COMPOUNDS, OXIDANTS

4623. Iodine(VII) oxide
[12055-24-2] **I_2O_7**



Diethyl ether
Mishra, H. C. *et al. J. Chem. Soc.*, 1962, 1195—1196
Washing of the (incompletely characterised) solid with ether occasionally led to explosive decomposition.
See other HALOGEN OXIDES, IODINE COMPOUNDS, OXIDANTS

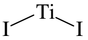
4624. Phosphorus diiodide triselenide
[30911-12-7] **$I_2P_4Se_3$**

$P_4I_2Se_3$

Nitric acid
See Nitric acid: Phosphorus compounds
See related IODINE COMPOUNDS, NON-METAL HALIDES, NON-METAL SULFIDES

4625. Titanium diiodide

[13783-07-8] **I_2Ti**



Preparative hazard

Gibson, 1969, 63

It may ignite in moist air.

See Titanium: Halogens (reference 3)

See other METAL HALIDES, PYROPHORIC MATERIALS

4626. Tungsten diiodide

[13470-17-2] **I_2W**

I—W—I

Preparative hazard

Mussell, R. D. *et al., Inorg. Chem.*, 1990, **29**(19), 3711

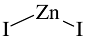
Explosions sometimes resulted on opening sealed tubes in which complex mixed halide salts of this compound had been prepared. There is no obvious source of pressure in the reaction mixture of dipotassium tetradecachlorotungstate, lithium iodide and potassium iodide.

See also Tungsten dichloride

See other METAL HALIDES

4627. Zinc iodide

[10139-47-6] **I_2Zn**



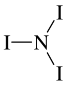
Sulfuric acid

See Sulfuric acid: Zinc iodide

See other METAL HALIDES

4628. Nitrogen triodide (Nitrogen iodide)

[13444-85-4] **I_3N**



Klapötke, T. M. *et al., Angew. Chem. (Int.)*, 1990, **29**(6), 677

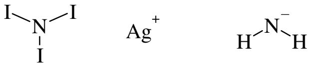
The uncomplexed material has been prepared and is very explosive, decomposing spontaneously at 0°C or below. Like its bromine and chlorine analogues, it is highly endothermic.

See next two below

See other ENDOTHERMIC COMPOUNDS, N-HALOGEN COMPOUNDS, IODINE COMPOUNDS

4629. Nitrogen triiodide—silver amide

[ ] **$I_3N.AgH_2N$**



Mellor, 1967, Vol. 8. Suppl. 2, 418

The dry complex may explode.

See other N-HALOGEN COMPOUNDS, IODINE COMPOUNDS, N-METAL DERIVATIVES, SILVER COMPOUNDS

4630. Nitrogen triiodide—ammonia

[34641-74-2], [14014-86-9] (1:1) **$I_3N.H_3N$**

Alone, or Halogens, or Oxidants, or Concentrated acids

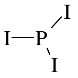
1. Mellor, 1940, Vol. 8, 607; 1967, Vol. 8, Suppl. 2, 418
2. Garner, W. E. *et al., Nature*, 1935, **135**, 832
3. Taylor, G. N., *Chem. Brit.*, 1981, **17**, 107
4. Houben-Weyl, 1977, Vol. 5.2a, 605
5. Bodner, G. M., *J. Chem. Educ.*, 1985, **62**(12), 1107
6. Bentzinger, von R. *et al., Praxis Naturwiss. Chem.*, 1987, **36**, 37

Readily formed in systems containing ammonia and iodine or some of its derivatives, the addition compound of nitrogen triiodide and ammonia when dry is an extremely sensitive, unstable detonator capable of initiation by minimal amounts of any form of energy (light, heat, sound, nuclear radiation, mechanical vibration), even at sub-zero temperatures, and occasionally even with moisture present. It may be handled cautiously when wet, but heavy friction will still initiate it. It explodes in boiling water and is decomposed by cold water to explosive diiodamine. It explodes, possibly owing to heat-initiation on contact with virtually any conc. acid, with chlorine or bromine, ozone or hydrogen peroxide solution [1]. Crystals desiccated in vacuum spontaneously explode when dry [2]. It has been formed in relatively large amounts during preparation of iodoacetylene derivatives in liquid ammonia [3][4], and may be destroyed by addition of sodium ethoxide [4]. Accidents involving demonstration of the explosive properties have been summarised [5]. A student prepared some to spread about on the floor as a joke, but it exploded prematurely while still in contact with the solution, causing eye injuries to the joker [6].

See other N-HALOGEN COMPOUNDS, IODINE COMPOUNDS

4631. Phosphorus triiodide

[13455-01-1] **I_3P**



Hydroxylic compounds, or Oxygen

Leleu, *Cahiers*, 1974, (75), 273

Interaction with water or glycerol is violent, and the iodide ignites in oxygen.

Sulfur acids

Dillon, K. B. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 887—888

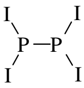
Contact with 25 or 50% oleum led to violently exothermic reactions, and vigorous reaction with chlorosulfuric acid.

See Phosphorus tribromide: Sulfur acids
Phosphorus trichloride: Sulfur acids

See other HALOPHOSPHINES, IODINE COMPOUNDS, NON-METAL HALIDES

4632. Tetraiododiphosphane

[13455-00-0] **I_4P_2**



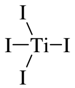
Preparative hazard

See Phosphorus: Halogens (references [3,4])

See other HALOPHOSPHINES, IODINE COMPOUNDS, NON-METAL HALIDES

4633. Titanium tetraiodide

[7720-83-4] **I_4Ti**



Preparative hazard

Denes, G., *J. Solid State Chem.*, 1988, **77**(1), 54—59

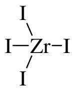
Use of a ‘bent copper tube’ reactor to prepare the iodide is hazardous.

See Titanium: Halogens

See other METAL HALIDES

4634. Zirconium tetraiodide

[13986-26-0] **I_4Zr**



Ethanol
Pascal, 1963, Vol. 9, 565
Interaction is very violent.
See other METAL HALIDES

4635. Indium
[7440-74-6] **In**

In

Acetonitrile, Dinitrogen tetraoxide
See Dinitrogen tetraoxide: Acetonitrile, etc.

Mercury(II) bromide
See Mercury(II) bromide: Indium

Sulfur
See Sulfur: Metals
See other METALS

4636. Indium(II) oxide
[12136-26-4] **InO**

$In^{2+} \quad O^{2-}$

Ellern, 1968, 33
The lower oxide, prepared by hydrogenation, incandesces on exposure to air.
See other METAL OXIDES, PYROPHORIC MATERIALS

4637. Indium phosphide
[22398-80-7] **InP**

InP

Preparative hazard
See Phosphorus: Metals
See METAL PNICTIDES

4638. Iridium
[7439-88-5] **Ir**

Ir

The finely divided catalytic metal may be pyrophoric.
See Zinc: Catalytic metals
See entry HYDROGENATION CATALYSTS

Interhalogens

See Bromine pentafluoride: Acids, etc.
Chlorine trifluoride: Metals

See other METALS, PYROPHORIC METALS

4639. Iridium(IV) oxide

[12030-49-8] **IrO_2**

$O{=}Ir{=}O$

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

See other METAL OXIDES

4640. Potassium

[7440-09-7] **K**

K

FPA H38, 1975; *HCS 1980*, 759

1. Gilbert, H. N., *Chem. Eng. News*, 1948, **26**, 2604
2. Johnson, W. S. *et al., Org. Synth.*, 1963, Coll. Vol. 4,134—135
3. *MCA Case History No. 1891*
4. Taylor, D. A. H., *Chem. Brit.*, 1974, **10**, 101
5. Diaper, D. G. M., *Chem. Brit.*, 1974, **10**, 312

5a. Anon., *Fire Precaut.*, 1988, (213), 46

6. Houben-Weyl, 1970, Vol. 13.1, 264
7. Burfield, D. R. *et al., Chem. & Ind.*, 1979, 89
8. Davis, A. C., *Chem. Brit.*, 1979, **15**, 179
9. Levy, J. *et al., Angew. Chem. (Intern. Ed.)*, 1981, **20**, 1033
10. Mellor, 1941, Vol. 2, 468; 1963, Vol. 2, Suppl. 2.2, 1559
11. Mellor, 1941, Vol. 2, 493
12. Short, J. F., *Chem. & Ind.*, 1964, 2132
13. Brazier, A. D., *Chem. & Ind.*, 1965, 220; Balfour, A. E., ibid., 353; Bil, M. S., ibid., 812; Cole, R. J., ibid., 944
14. March, R. G., *Chem. Brit.*, 1979, **15**, 65
15. Brock, T. H. *et al., Nachr. Chem. Tech. Lab.*, 1998, **46**(1), 16
16. Brandsma, 1971, 10, 21
17. Klapoetke, T. *et al., Chem. Brit.*, 2002, **38**(9), 21; *Chem. Eng. News*, 2002, 80(37), 4

In a review of the comparative properties of sodium and potassium, the latter is rated as invariably the more hazardous [1]. Laboratory procedures for safe handling of potassium have been detailed [2]. A safe method for disposal of potassium residues in bulk storage and processing vessels has been developed. Basically the method involves reaction of the metallic residues with dry (condensate-free) steam under closely controlled conditions. It may be used where small-scale techniques (dissolution in higher alcohols) are inapplicable [3]. Hazards associated with storage of potassium in aluminium containers are discussed. The severe corrosion leading to perforation of such commercially supplied containers [4] was attributed to the deliquescent and subsequently corrosive nature of potassium carbonate formed from atmospheric carbon dioxide inside the container. Sodium may be safely stored in aluminium cans because the derived sodium carbonate is not deliquescent and causes no corrosion [5]. A serious laboratory fire originating in a store cupboard containing potassium in an aluminium container may have arisen through corrosive failure of the latter [5a]. There is a considerable risk of fire if powdered potassium ('potassium sand') dispersed in benzene is exposed to air [6]. A practical survey of methods of safe handling and disposal of potassium covers the separation of metal from adhering oxide by melting under xylene containing 1% of isopropanol, disposal of small metal residues by treatment with 1:1 ethyl acetate—hydrocarbon diluent mixtures, and disposal of 30 g blocks by dropping into a 2 m deep hole in the ground containing 0.5 m of water [7]. Several fires (but not explosions) occurred when potassium was 'blotted' free of solvent (used to remove traces of oil) with previously used filter paper. The fires were attributed to rapid formation of potassium hydroxide solution from traces of potassium on the filter paper under humid conditions, and ignition of the dry metal on contact with the wet alkali [8]. Potassium dispersed on silica is relatively air stable [9], unlike the dispersions on sodium carbonate or potassium carbonate which are pyrophoric.

It is convenient to consider interaction of potassium and air under two headings.

Rapid oxidation

Reaction with air or oxygen in complete absence of moisture does not occur, even on heating to the boiling point. However, in contact with normal (moist) air, oxidation may become so fast that melting or ignition occurs, particularly if pressure is applied locally to cause melting and exposure of a fresh surface, as when potassium is pressed through a die to form potassium wire [10].

Slow oxidation

Metallic potassium on prolonged exposure to air forms a coating of yellowish potassium superoxide (KO_2) under which is a layer of potassium oxide in contact with the metal [11]. The previous statements that normal contact of potassium with the superoxide causes ignition to occur [11], and that if the layer of superoxide is impacted into the underlying metal by dry cutting operations or a hammer blow an explosion occurs [1,12] are now known to be incorrect. The explosions are caused by interaction of residual traces of mineral oil or other organic contaminant, rather than potassium metal, with the surface layer of superoxide, initiated by the blade pressure or impact. Cases of flashes of light and fires [13] or explosion [14] when potassium (some were old samples) was cut under oil have been reported. A review with references on explosion hazards of potassium, gives particular attention to oxidised crusts [15]. A fatal explosion occurred when potassium stored in vacuum sealed polythene film was melted in an alkane solvent at 90°C. Investigation of similar material showed the crust to lack peroxides, in the strict sense, with about 15% potassium superoxide by weight, but to consist mostly of potassium hydroxide monohydrate. It is postulated that explosion may also be caused by interaction of molten metal with the available water. [Polythene is permeable to water vapour – Ed.] [17]

Fresh potassium should be stored under dry xylene in airtight containers to prevent oxidation [11]. Old stocks, where the coating is orange or yellow, should not be cut, but destroyed by burning on an open coke fire, or by addition of *tert*-butanol to small portions under xylene in a hood. It is dangerous to use methanol or ethanol (either wet or dry) as a replacement for *tert*-butanol. Recommended procedures include cutting and handling the metal with forceps under dry xylene, and disposal of scraps in xylene by addition of *tert*-butanol [1,12,13], even the latter being capable of violent reaction [16]. Alternatively, ethyl acetate—hydrocarbon mixtures may be used for small disposals [7].

See Potassium dioxide (reference 3)

See Potassium—sodium alloy

Acetylene

See Acetylene: Potassium

See other CORROSION INCIDENTS

Alcohols

Pratt, E. F. *et al., J. Amer. Chem. Soc.*, 1954, **75**, 54

Interaction with a range of alcohols (n-propanol to n-octanol, benzyl alcohol, cyclohexanol) to form the alkoxides usually led to explosions unless air in the containing vessel was displaced by nitrogen before addition of potassium in small portions with stirring.

See Slow oxidation, above

Aluminium, Air

Anon., *Fire Prevention*, 1988, (213), 46

After a fire which started in a disused fume cupboard employed as a storage space for various inorganic chemicals, including potassium, it is suggested that the potassium oxides which inevitably coat aged potassium may have corroded the aluminium can, releasing the oil in which the metal is stored and exposing it to accelerated oxidation. This argument is thermodynamically sound, but kinetically questionable as it involves a solid/solid interaction of potassium and aluminium oxides.

Carbon

1. Mellor, 1963, Vol. 2, Suppl. 2.2, 1566
2. Mellor, D. P., *Chem. & Ind.*, 1965, 723
3. *Alkali metals*, 1957, 169

Reaction of various forms of carbon (soot, graphite or activated charcoal) is exothermic and vigorous at elevated temperatures, and if the carbon is finely divided and air is present, ignition may occur leading to explosions, possibly owing to the potassium superoxide which would be formed [1]. Explosions caused by attempts to extinguish potassium fires with graphite powder have been so attributed [2]. Potassium cannot be produced by electrolysis of potassium chloride because of interaction of the metal with graphite electrodes and formation of explosive 'carbonylpotassium' (potassium benzenehexoxide) [3].

Carbon disulfide

See Carbon disulfide: Alkali metals

Dimethyl sulfoxide
See Dimethyl sulfoxide: Potassium

Ethylene oxide MRH 3.72/99+
See Ethylene oxide: Contaminants

Halocarbons MRH values below references

1. Staudinger, H., *Z. Angew. Chem.*, 1922, **35**, 657
2. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
3. Lenze, F. *et al. Chem. Ztg.*, 1932, **56**, 921
4. Rampino, L. D., *Chem. Eng. News*, 1958, **36**(32), 62

MRH Bromoform 3.14/68, carbon tetrachloride 5.19/50, chloroform 4.93/50, pentachloroethane 4.98/51, tetrachloroethane 4.77/52, tetrachloroethylene 5.23/51

Although apparently stable on contact, mixtures of potassium (or its alloys) with a wide range of halocarbons are shock-sensitive and may explode with great violence on light impact. Chloroethane, dichloroethane, trichloroethane, pentachloroethane, bromoform, dibromomethane and diiodomethane are among those investigated. Sensitivity increases generally with the degree of substitution, and potassium—sodium alloy gives extremely sensitive mixtures. The mixture with carbon tetrachloride is 150—200 times as shock-sensitive as mercury fulminate, and a mixture of potassium with bromoform was exploded by a door slamming nearby [1][2]. Mixtures with tetrachloroethane and pentachloroethane will often explode after a short delay during which a voluminous solid separates out [3]. When heated together, potassium and tetrachloroethylene exploded at 97—99°C, except when the metal had been very recently freed of its usual oxide film. Sodium did not explode under the same conditions [4].

See Oxalyl dihalides, below

Halogens or Interhalogens MRH Bromine 3.22/68, chlorine 5.77/48

1. Mellor, 1941, Vol. 2, 114, 469; 1963, Vol. 2, Suppl. 2.2, 1563
2. Pascal, 1960, Vol. 16, 578

Potassium ignites in fluorine and in dry chlorine (unlike sodium). In bromine vapour it incandesces, and explodes violently in liquid bromine. Mixtures with iodine incandesce on heating, and explode weakly on impact. Potassium reacts explosively with molten iodine bromide and iodine, and a mixture with the former is shock-sensitive and explodes strongly. Molten potassium reacts explosively with iodine pentafluoride [1]. Contact with iodine trichloride causes ignition [2].

Hydrazine
See Hydrazine: Potassium

Hydrogen halides MRH Hydrogen chloride 3.72/48

1. Cueilleron, J., *Bull. Soc. Chim. Fr.*, 1945, **12**, 88
2. Pascal, 1963, Vol. 2.2, 31

Impact causes a mixture of potassium and anhydrous hydrogen chloride to explode very violently [1]. Molten potassium ignites in contact with hydrogen chloride, hydrogen bromide or hydrogen iodide [2].

Magnesium halides, Potassium iodide

Rieke, R. D. *et al., Org. Synth.*, 1979, *59*, 85—94

Interaction of potassium with magnesium bromide, magnesium chloride or magnesium iodide in refluxing THF produces very finely divided and highly reactive magnesium which will ignite if exposed long to air.

See PYROPHORIC METALS

Maleic anhydride

See Maleic anhydride: Bases, etc.

Mercury

Mellor, 1941, Vol. 2, 469

Interaction to form amalgams is vigorously exothermic and may become violent if too much potassium is added at once.

Metal halides

MRH Cobalt(II) chloride 2.59/62, iron(II) bromide 1.80/74, iron(III) bromide 1.88/72, iron(III) chloride 3.22/58, iron(II) iodide 1.38/80, aluminium chloride 2.43/53, copper(I) chloride 2.18/72, copper(II) chloride 3.10/63, silver fluoride 2.18/76

1. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
2. Cueilleron, J., *Bull. Soc. Chim. Fr.*, 1945, **12**, 88
3. Mellor, 1963, Vol. 2, Suppl. 2.2, 1571
4. Rieke, R. D., *Accts. Chem. Res.*, 1977, **10**, 301—305

Mixtures of potassium with metal halides are sensitive to mechanical shock, and the ensuing explosions have been graded. Very violent explosions occurred with calcium bromide, iron(III) bromide, iron(III) chloride, iron(II) bromide, iron(II) iodide or cobalt(II) chloride. Strong explosions occurred with silver fluoride, mercury(II) bromide, mercury(II) chloride, mercury(II) fluoride, mercury(II) iodide, copper(I) bromide, copper(I) chloride, copper(I) iodide, copper(II) bromide, copper(II) chloride, and ammonium tetrachlorocuprate; zinc and cadmium chlorides, bromides and iodides; aluminium fluoride, chloride, or bromide, thallium(I) bromide; tin(II) or (IV) chloride, tin(IV) iodide (with sulfur), arsenic trichloride and triiodide, antimony and bismuth tribromides, trichlorides and triiodides; vanadium(V) chloride, chromium(IV) chloride, manganese(II) and iron(II) chlorides, and nickel bromide, chloride or iodide. Weak explosions occurred with a wide variety of other halides [1,2,3]. These reactions may be moderated by the use of ether or hydrocarbon solvents. The reactions are still highly exothermic but controllable, and give finely divided and highly reactive metals, some pyrophoric in air, such as magnesium and aluminium [4].

See Magnesium halides, etc., above

Metal oxides

1. Mellor, 1963, Vol. 2, Suppl. 2.2, 1571
2. Mellor, 1941, Vol. 3, 138
3. Mellor, 1940, Vol. 4, 770, 779
4. Mellor, 1941, Vol. 7, 401
5. Mellor, 1943, Vol. 11, 237, 542
6. Mellor, 1941, Vol. 9, 649

Lead peroxide reacts explosively [1] and copper(II) oxide incandescently [2] with warm potassium. Mercury(II) and (I) oxides react with molten potassium with incandescence and explosion, respectively [3]. Tin(IV) oxide is reduced incandescently on warming [4] and molybdenum(III) oxide on heating [5]. Warm bismuth trioxide is reduced with incandescence [6].
See 'Mercury(I) oxide': Alkali metals

Nitric acid
Pascal, 1963, Vol. 2.2, 31
Interaction with conc. nitric acid is explosive.

Nitrogen-containing explosives
Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
Nitro or nitrate explosives, normally shock-insensitive, are rendered extremely sensitive by addition of traces of potassium or potassium—sodium alloy. Ammonium nitrate, and nitrate—sulfate mixtures, picric acid, and even nitrobenzene respond in this way.

Non-metal halides
1. Mellor, 1963, Vol. 2, Suppl. 2.2, 1564—1568
2. Mellor, 1940, Vol. 8, 1006
3. Mellor, 1947, Vol. 10, 642—646, 908, 912

Diselenium dichloride and seleninyl chloride both explode on addition of potassium [1,3], while the metal ignites in contact with phosphorus trichloride vapour or liquid [2]. Mixtures of potassium with sulfur dichloride or sulfur dibromide, phosphorus tribromide or phosphorus trichloride, and with phosgene are shock-sensitive, usually exploding violently on impact. Potassium also explodes violently on heating with disulfur dichloride, and with sulfur dichloride or seleninyl bromide without heating [3].

Non-metal oxides MRH Dinitrogen oxide 3.72/54, nitrogen oxide 4.60/61
1. Gilbert, H. N., *Chem. Eng. News*, 1948, **26**, 2604
2. Mellor, 1941, Vol. 2, 241
3. Mellor, 1940, Vol. 8, 436, 544, 554, 945
4. Pascal, 1963, Vol. 2.2, 31

Mixtures of potassium and solid carbon dioxide are shock-sensitive and explode violently on impact, and carbon monoxide readily reacts to form explosive 'carbonylpotassium' (potassium benzenehexoxide) [1]. Dichlorine oxide explodes on contact with potassium [2]. Potassium ignites in dinitrogen tetraoxide or dinitrogen pentaoxide at ambient temperature and incandesces when warmed with nitrogen oxide or phosphorus(V) oxide [3]. At —50°C, potassium and carbon monoxide react to give dicarbonylpotassium, which explodes in contact with air or water, or at 100°C. At 150°C, the product is a trimer of this, potassium benzenehexoxide. The just-molten metal ignites in sulfur dioxide [4].

Organic samples for qualitative analysis
See LASSAIGNE TEST (reference 2)

Other reactants

Yoshida, 1980, 96—97

MRH values calculated for 49 combinations with a wide variety of other materials are given.

Oxalyl dihalides

Staudinger, H., *Z. Angew. Chem.*, 1922, **35**, 657; *Ber.*, 1913, **46**, 1426

In absence of mechanical disturbance, potassium or potassium—sodium alloy appears to be stable in contact with oxalyl dibromide or oxalyl dichloride, but the mixtures are very shock-sensitive and explode very violently.

See Halocarbons, above

Oxidants

Mellor, 1963, Vol. 2, Suppl. 2.2, 1571

The potential for violence of interaction between the powerful reducing agent potassium and oxidant classes has been well described. Other miscellaneous oxygen-containing substances which react violently or explosively include sodium iodate, silver iodate, lead sulfate and boric acid.

See Metal oxides
  Ammonium nitrate: Ammonium sulfate, etc.
  Chlorine trifluoride: Metals
  Chromium trioxide: Alkali metals
  Dichlorine oxide: Oxidisable materials
  Nitryl fluoride: Metals
See Selenium, etc., below
See also Non-metal oxides, above
See also Sulfur, below
See also Sulfuric acid, below

Selenium, or Tellurium

Mellor, 1947, Vol. 10, 767; 1943, Vol. 11, 40

Interaction of selenium and potassium is exothermic and ignition occurs, or, with excess potassium, a slight explosion. Tellurium and potassium become incandescent when warmed in a hydrogen atmosphere to prevent aerobic oxidation.

Sulfur

Pascal, 1963, Vol. 2.2, 30

Interaction is violent on warming.

Sulfuric acid MRH 3.57/56

Kirk-Othmer, 1961, Vol. 16, 362

Interaction is explosive.

Water

1. Mellor, 1941, Vol. 2, 469; 1963, Vol. 2, Suppl. 2.2, 1560
2. Angus, L. H., *School Sci. Rev.*, 1950, **31**(115), 402
3. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633—636
4. Ashman, A., *School Sci. Rev.*, 1983, **65**(231), 387

Interaction is violently exothermic, and the heat evolved with water at 20°C is enough to ignite evolved hydrogen. Larger pieces of potassium invariably explode in water and scatter burning potassium particles over a wide area. Aqueous alcohols should not be used for waste metal disposal [1]. Small pieces of potassium will also explode with a restricted amount of water [2]. The reactivity of potassium and other alkali metals with water has been discussed in detail. The vigour of reaction is scarcely reduced by contact with ice—water slurries [3]. A convenient demonstration of ignition of potassium by placing a small piece on an ice cube is due to Faraday [4].
See ALKALI METALS, REDUCANTS
See other METALS

4641. Potassium—sodium alloy

[12532-69-3] **K—Na**

K—Na

1. *Health and Safety Information*, 251, Washington, USAEC, 1967
2. Ellis, J. E. *et al., Inorg. Synth.*, 1976, **16**, 70
3. Mellor, 1961, Vol. 2, Suppl. 2.1, 562
4. Anon., *Fire Prot. Assoc. J.*, 1965, **68**, 1402

Appropriate precautions in handling the alloy, used as a thermally stable and radiation-resistant liquid coolant for reactor cores, are described. It is generally more hazardous than either of the component metals, because alloys in the range 50—80 wt% of potassium are liquid at ambient temperature and can therefore come into more intimate contact with reagents than the solid metals. Most of the entries under Potassium above, and some of those under Sodium may be expected to apply to their alloys, with allowance for the composition [1]. For the destruction of residual small amounts of the alloy, treatment with a 1:1 mixture of isopropanol and heptane over a safety tray is recommended [2]. The alloy usually ignites on exposure to air, with which it reacts in any case to form potassium dioxide (or superoxide), a very powerful oxidant [3]. Fires may be extinguished with dried sodium carbonate, calcium carbonate, sand or resin-coated sodium chloride. Graphite is not suitable as violent reaction with the superoxide is possible. Carbon dioxide or halocarbon extinguishers must not be used, to avoid explosions [4].
See Carbon dioxide
See Potassium dioxide: Carbon
See also Halocarbons, below

tert-Butanol
Renfrew, M. M., *J. Chem. Educ.*, 1983, **60**, A229
Contact of the alloy with *tert*-butanol caused ignition.
See reference 2, main entry above

Carbon dioxide
Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
Mixtures of the alloy and solid carbon dioxide are powerful explosives, some 40 times more sensitive to shock than mercury fulminate.

Carbon disulfide

See Carbon disulfide: Alkali metals

Fluoropolymers

1. *491M*, 1975, 394
2. Kimura, T. *et al., J. Chem. Educ.*, 1973, **50**, A85

Poly-tetrafluoroethylene or -hexafluoropropylene sealing tapes burned vigorously in contact with the alloy in a helium atmosphere [1]. A teflon-coated magnetic stirrer bar used to stir the alloy under propane atmosphere ignited when the speed was increased and generated enough heat to melt the glass. Triboelectric initiation was postulated [2].

See other GLASS INCIDENTS

Halocarbons

1. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 550
2. *Inform. Exch. Bull.*, Lawrence Radiation Lab., 1961, **1**, 22
3. Schmidt, E. *et al., Chem. Abs.*, 1975, **83**, 163034
4. *491M*, 1975, 394

The liquid alloy gives mixtures with halocarbons even more shock-sensitive than those with potassium. Highly chlorinated methane derivatives are more reactive than those of ethane, often exploding spontaneously after a delay [1]. Contact of 1,1,1-trichloroethane with a trapped alloy residue in a valve caused an explosion [2]. It is to be expected that chlorofluorocarbons will also form hazardous mixtures in view of their reactivity with barium. Precautionary measures for demonstrating the explosion of the alloy with chloroform are detailed [3]. Addition of 2 drops of 1,1,2-trichlorotrifluoroethane to the alloy caused a violent explosion [4].

See Fluoropolymers, above

See other METAL—HALOCARBON INCIDENTS

Metal halides

1. Rieke, R. D., *Accts. Chem. Res.*, 1977, **10**, 302
2. Ellern, 1968, 43

Use of the alloy to reduce metal halides in solvents to the finely divided and highly reactive metals is not recommended for cases where the halide is highly soluble in the solvent (e.g. zinc chloride or iron(III) chloride in THF). Explosive reaction may ensue [1]. The alloys explode violently in contact with silver halides.

See Potassium: Metal halides

Metal oxides

Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 551

Mixtures of the alloy with silver oxide or mercury oxide are shock-sensitive powerful explosives. The red form of mercury(I) oxide gives mixtures 40 times, and the yellow form 140 times as sensitive as mercury fulminate.

Nitrogen-containing explosives

See Potassium: Nitrogen-containing explosives

Non-metal halides

U.S. Office of Nuclear and Facility Safety, Operating Experience Weekly Summary, 95-23, 1995

Not surprisingly, an explosion resulted on mixing with ‘silicon chloride’. This sprayed unreacted metal, which later ignited, casuing a small fire. [All non-metal halides are likley to react violently, any unreactivity can only be kinetic. – Ed.]

Water

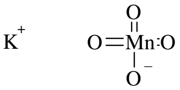
Anon., *Loss Prev. Bull.*, 1977, (018), 18

The liquid alloy was used in an unlabelled Dreschel bottle to dry inert gas. A violent explosion occurred when the bottle was being cleaned, owing to contact of the alloy with water. Other desiccants are much safer (and would avoid the possibility of mistaking the alloy for mercury).

See other ALLOYS, PYROPHORIC MATERIALS

4642. Potassium permanganate

[7722-64-7] **$KMnO_4$**



FPA H28, 1974; *HCS 1980*, 774

Acetic acid, or Acetic anhhydride MRH 2.34/84 / 2.55/86

von Schwartz, 1918, 34

Cooling is necessary to prevent possible explosion from contact of potassium permanganate (or the sodium or calcium salts) with acetic acid or acetic anhydride.

See Oxygenated organic compounds, below

Acetone, *tert*-Butylamine MRH Acetone 2.76/8

1. Kornblum, N. *et al., Org. Synth.*, 1973, Coll. Vol. 5, 847
2. Kornblum, N. *et al., Org. Synth.*, 1963, **43**, 89
3. Haynes, R. K. *et al., Lab. Equip. Digest*, 1974, **12**(6), 98; private comm., 1974

In the reprinted description [1] of a general method of oxidising *tert*-alkylamines to the corresponding nitroalkanes, a superscript reference indicating that *tert*-butylamine should be oxidised in water alone, rather than in acetone containing 20% of water, is omitted, although it was present in the original description [2]. This appears to be important, because running the reaction in 20% aqueous acetone led to a violent reaction with eruption of the flask contents. This was attributed to caking of the solid permanganate owing to inadequate agitation, and onset of an exothermic reaction between oxidant and solvent [3].

Alcohols, Nitric acid

Numjal, N. L. *et al., Amer. Inst. Aero. Astronaut. J.*, 1972, **10**, 1345

Methanol, ethanol, isopropanol, pentanol or isopentanol do not ignite immediately upon mixing with red fuming nitric acid, but addition of potassium permanganate (20%) to the acid before mixing causes immediate ignition.

See Nitric acid: Alcohols

Aluminium carbide
Mellor, 1946, Vol. 5, 872
Incandescence on warming.

Ammonia, Sulfuric acid
Mellor, 1941, Vol. 1, 907
Ammonia is oxidised with incandescence in contact with the permanganic acid formed in the mixture.

Ammonium nitrate
Urbanski, 1965, Vol. 2, 491
A mixture of 0.5% of potassium permanganate with an ammonium nitrate explosive caused an explosion 7 h later. This was owing to formation and exothermic decomposition of ammonium permanganate, leading to ignition.

Ammonium perchlorate
See Ammonium perchlorate: Impurities

Antimony, or Arsenic MRH 0.25/86, 0.25/91, resp.
Mellor, 1942, Vol. 12, 322
Antimony ignites on grinding in a mortar with the solid oxidant, while arsenic explodes.

Coal, Peroxomonosulfuric acid
Rawat, N. S., *Chem. & Ind.*, 1976, 743
In a new method for determination of sulfur in coal, the samples are oxidised with an aqueous mixture of permanganate and the peroxoacid. During the digestion, a reflux condenser is essential to prevent loss of water, which could lead to explosively violent oxidation.

Dichloromethylsilane
See Dichloromethylsilane: Oxidants

Dimethyl sulfoxide MRH 3.01/86
Kirk-Othmer (3rd ed.), 1982, Vol. 19, 494
The solvent ignites in contact with the solid oxidant.
See Oxygenated organic compounds, below

Dimethylformamide
Finlay, J. B., *Chem. Eng. News*, 1980, **58**(38), 65
Addition of potassium permanganate to dimethylformamide to give a 20% (approx. saturated) solution led to an explosion after 5 min. Subsequent tests on 1 g of oxidant with 5 g of solvent showed a rapid exotherm after 3—4 min, accompanied by popping noises from undissolved oxidant.
See Oxygenated organic compounds, below
See also Dimethylformamide: Oxidants

Ethanol, Sulfuric acid
Koch, K. R., *J. Chem. Educ.*, 1982, **58**, 973—974

In a demonstration of the powerful oxidant effect of manganese heptoxide on ethanol layered on top of sulfuric acid, it is essential to observe all the precautions given to prevent violent exothermic reactions.

Formaldehyde

1. Piefel, W. *et al., Chem. Abs.*, 1977, **86**, 60508
2. Robinson, P. J., *Chem. & Ind.*, 1978, 723
3. Wainmann, H. E., *Chem. & Ind.*, 1978, 744
4. Craven, J. R., *Chem. Brit.*, 1979, **15**, 66
5. Young, J. A., *CHAS Notes*, 1988, **6**(3), 6

Formaldehyde gas for disinfection purposes may be released from the aqueous solution ('formalin') by treatment with potassium permanganate (the heat for evaporation arising from the redox reaction), but the quantities must be limited to avoid the risk of fire or explosion [1]. There is an account of an incident involving an extremely exothermic reaction overnight after addition of 0.1 l of formalin to 50 g of oxidant in a plastic beaker, which was melted [2]. Electrically heated evaporation of formalin is a safer fumigation technique [3]. The wisdom of using plastic containers for any unsupervised exothermic reaction is questioned [4]. An attempt to disinfect a large building and its hundreds of incubators all at once by running formalin from a 180 l drum onto several kg of potassium permanganate in a small waste container led, predictably, to a large fire which destroyed the building and its contents [5].

Glycerol

1. 'Leaflet No. 5', London, Inst. of Chem., April, 1940
2. Anon., *BCISC Quart. Safety Summ.*, 1974, **45**, 11—122
3. Bozzelli, J. W. *et al., J. Chem. Educ.*, 1979, **56**, 675—676
4. Kauffman, G. B. *et al., J. Chem. Educ.*, 1981, **58**, 802

Contact of glycerol with solid potassium permanganate caused a vigorous fire [1]. During the preparation of a solution for the decontamination of tetramethyllead spills, addition of the solid oxidant to a bucket contaminated with glycerol caused ignition to occur after a few s [2]. The trifunctionality and high viscosity of glycerol give high heat release and poor dissipation of reaction heat, respectively. The combination is a reliable method of igniting thermite mixture demonstrations [3], which should be conducted out of doors [4].

See Oxygenated organic compounds, below

Hydrochloric acid MRH 0.75/63

1. Curry, J. C., *School Sci. Rev.*, 1965, **46**(160), 770
2. Adair, A., *Chem. & Ind.*, 1965, 1723
3. Jenkins, E. W., private comm., 1976
4. Ephraim, 1939, 162

During preparation of chlorine by addition of the conc. acid to solid permanganate, a sharp explosion occurred on one occasion [1]. Sulfuric acid was not used in error, nor was tube blockage involved [2]. A similar incident was reported later [3]. It appears remotely possible that permanganate may be able to oxidise chlorine to chlorine oxide [4], which as a dilute mixture with chlorine would be mildly explosive in the gas phase.

Hydrofluoric acid

Black, A. M. *et al., J. Chem. Soc., Dalton Trans.*, 1974, 977

During preparation of potassium hexafluoromanganate(IV), addition of the solid oxidant to exceptionally conc. hydrofluoric acid (60—90%, rather than 40% previously used) caused a violent exotherm with light emission.

Hydrogen peroxide

Anon., *J. Pharm. Chim.*, 1927, **6**, 410

Contact of hydrogen peroxide from a broken bottle with pervious packages of permanganate caused a violent reaction and fire.

See Hydrogen peroxide: Metals, etc. (reference 3)

Hydrogen trisulfide

Mellor, 1947, Vol. 10, 159

Contact with solid permanganate ignites the liquid sulfide.

Hydroxylamine MRH 3.85/99+

See other REDOX REACTIONS

Non-metals MRH values below reference

Mellor, 1942, Vol. 12, 319—323

MRH Carbon 2.59/7, phosphorus (yellow) 6.88/62, (red) 2.34/16, sulfur 2.80/12

A mixture of carbon and potassium permanganate is not friction-sensitive, but burns vigorously on heating. Mixtures with phosphorus or sulfur react explosively on grinding or heating, respectively.

Organic nitro compounds

Blinov, I., *J. Chem. Ind. USSR*, 1937, **14**, 1151—1153

Mixtures ignite easily on heating, shock, or contact with sulfuric acid.

Other reactants

Yoshida, 1980, 90

MRH values calculated for 26 combinations with oxidisable materials are given.

Oxygenated organic compounds MRH values below references

1. Rathsbury, H. *et al., Chem. Ztg.*, 1941, **65**, 426—427
2. Gallais, 1957, 697
3. Partington, 1967, 830—831

Contact of several liquid organic compounds, or of aqueous solutions of solids, with the powdered oxidant leads to ignition. Presence of hydroxy and /or keto groups causes an extraordinary increase in sensitivity. Such compounds include ethylene glycol, propane-1,2-diol, erythritol, mannitol, triethanolamine, 3-chloropropane-1,2-diol; acetaldehyde, isobutyraldehyde, benzaldehyde; acetylacetone; esters of ethylene glycol, lactic acid, acetic acid, oxalic acid. The necessary presence of hydroxy or keto groups may be connected with solubility factors [1]. Mixtures of the solid oxidant with solid reducing sugars may react violently or explosively [2]. Powdered oxalic acid and the oxidant ignite soon after mixing [3].

See Ethylene glycol: Oxidants

Polypropylene

MCA Case History No. 1842

While using a screw conveyor to move the solid oxidant, ignition of a polypropylene tube in the feed system occurred. This could not be reproduced, even when likely contaminants were present.

Potassium chloride, Sulfuric acid

491M, 1975, 347

An attempt to prepare permanganyl chloride by cautiously adding conc. sulfuric acid to an intimate mixture of the salts at 0°C in clean glass apparatus caused a violent explosion.

Reducants

Interaction may be violent or explosive.

See Formaldehyde, above
Hydrazine: Oxidants
Hydroxylamine: Oxidants

Slag wool

Hallam, B. J. *et al., School Sci. Rev.*, 1975, **56**(197), 820

Generation of oxygen by heating a layer of potassium permanganate retained in a test tube by a plug of 'Rocksil' slag wool led to minor explosions. The wool liberated an organic distillate on heating, and the explosions were attributed to combustion of the distillate in the liberated oxygen. Roasting the wool before using it with oxidants is recommended.

Sulfur

Fox, M. www.chemaxx.com/fires

A consultant's website reports a helicopter crash apaprently caused by insufficient cleaning of a tank between sulfur-dusting and permanganate application. Mixtures of the solids may ignite on modest friction [Editor's experience].

Sulfuric acid, Water

1. Archer, J. R., *Chem. Eng. News*, 1948, **26**, 205
2. Anon., *ABCM Quart. Safety Summ.*, 1946, **17**, 2
3. Stevens, G. C., private comm., 1971
4. Haight, G. P. *et al., Chem. Eng. News*, 1980, **58**(13), 3
5. Mann, L. T., *Chem. Eng. News*, 1980, **58**(18), 2
6. Gulick, W. M., *Chem. Eng. News*, 1980, **58**(28), 5
7. Olley, R. H., *J. Polym. Sci. Polym. Phys. Edn.*, 1979, **176**, 627
8. Olley, R. H., *Chem. Brit.*, 1988, **24**, 31
9. Anon., *Polymer*, 1982, **23**, 1707
10. Johansen, J. S. *et al., Dansk Kemi*, 2004, **85**(5), 14
11. Ceru, B. *Safe Science (Michigan State University)*, 1995, Dec.

Addition of conc. Sulfuric acid to the slightly damp permanganate caused an explosion. This was attributed to the formation of permanganic acid, dehydration to dimanganese heptoxide and explosion of the latter, caused by heat liberated from interaction of sulfuric acid and moisture [1]. A similar incident was reported previously when a solution of potassium permanganate in sulfuric acid, prepared as a cleaning agent, exploded violently [2]. An explosion, after a short induction period, when a solution was prepared by addition of acid to (dry?) permanganate is again reported [11]. There is, however a reputedly safe procedure for the final ultra-cleaning of glassware in cases where the adsorbed chromium film left by chromic acid cleaning would be intolerable. This involves treatment of the glassware with conc. Sulfuric acid (10 ml) to which one or two small crystals (not more) of permanganate have been added. If the solution changes to a brown colour, it must immediately be discarded into excess water [3]. A lecture demonstration of the 'permanganate volcano' involving preparation of manganese heptoxide exploded with great violence. It was concluded that the demonstration was too dangerous to use [4]. Similar comments followed [5,6]. When preparing a 7% solution of potassium permanganate in conc. Sulfuric acid as an etchant for polyalkenes, it is essential to use only small quantities and to stir the acid rapidly while adding the oxidant and until it is completely dissolved [7]. An attempt to do this with inadequate instructions (3 l of acid; no agitation) led to a violent explosion which demolished a fume cupboard [8]. A safer, more dilute etchant solution has been described [9]. An accident is reported during preparation of a similar solution for analytical purposes [10].

Titanium

Mellor, 1941, Vol. 7, 20

A mixture of powdered metal and oxidant explodes on heating.

Trifluoroacetic anhydride

1. Perrin, D. D. *et al., Purification of laboratory chemicals*, 448, Sydney, Pergamon, 2nd ed., 1980
2. Mook, R. A., *Chem. Eng. News*, 1987, **65**(13), 2
3. Author's comments

A bottle of the anhydride had been purified uneventfully by distillation from potassium permanganate according to a published procedure [1]. When a second batch was attempted, a brown colour was observed in the distillation flask and the distillate was green, so distillation was stopped. Several hours later the distillation flask exploded spontaneously and with great violence. This was attributed to the formation of dimanganese heptaoxide (which caused the brown colouration). Trifluoroacetic acid may also explode if the same purification procedure is followed [2]. It seems likely that the first bottle of anhydride had a low content of trifluoroacetic acid, so that little of the dimanganese heptaoxide would be produced by liberation of permanganic acid and its subsequent dehydration by the anhydride. If the second sample of anhydride had an appreciably higher acid content, a substantial amount of the explosive heptaoxide could have been produced during the several hours standing by the progressive reaction sequence below. [3]

$$2F_3CCO.OH + 2KMnO_4 \rightarrow 2HMnO_4 + 2F_3CO.OK$$

$$2HMnO_4 + (F_3CCO.)_2O \rightarrow Mn_2O_7 + 2F_3CCO.OH$$

3,4,4″-Trimethyldiphenyl sulfone

Adduci, J. M. *et al., Macromol. Synth.*, 1982, **8**, 53—56

During oxidation of the sulfone to the tricarboxylic acid, addition of oxidant must be in small portions to avoid an exothermic vigorous reaction.

Wood MRH Cellulose 2.68/15

1. Anon., *Chem. Ztg.*, 1927, **51**, 221
2. Dunn, B. W., *Amer. Rail Assoc., Bur. Explos., Rept. No. 10*, 1917

Contact between the solid oxidant and wood, in presence of either moisture [1] or mechanical friction [2] may cause a fire.

See other METAL OXOMETALLATES, OXIDANTS

4643. Potassium thiazate

[73400-02-9] **KNOS**

$K^{+} \quad N^{-}{=}S{=}O$

Alone, or Water

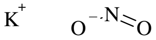
Armitage, D. A. *et al., J. Chem. Soc., Chem. Comm.*, 1979, 1078—1079

It explodes upon ignition dry, and ignites in contact with water.

See other N-METAL DERIVATIVES, N—S COMPOUNDS

4644. Potassium nitrite

[7758-09-0] **KNO_2**



HCS 1980, 772

Ammonium salts

Mellor, 1941, Vol. 2, 702

Addition of ammonium sulfate to the fused nitrite causes effervescence and ignition.

See NITRITE SALTS OF NITROGENOUS BASES

Boron

Mellor, 1946, Vol. 5, 16

Addition of boron to the fused nitrite causes violent decomposition.

Potassium amide

Bergstrom, F. W., *Chem. Rev.*, 1933, **12**, 64

Heating a mixture of the solids under vacuum causes a vigorous explosion.

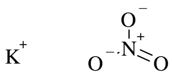
Potassium cyanide

See Sodium nitrite: Metal cyanides

See other METAL NITRITES, METAL OXONON-METALLATES, OXIDANTS

4645. Potassium nitrate

[7757-79-1] **KNO_3**



FPA H74, 1978; *HCS 1980*, 771

Aluminium, Barium nitrate, Potassium perchlorate, Water
See Aluminium: Metal nitrates, etc.

1,3-Bis(trichloromethyl)benzene
See 1,3-Bis(trichloromethyl)benzene: Oxidants

Boron, 'Laminac', Trichloroethylene
MCA Case History No. 745
A 14 kg batch of the mixture, mainly of boron and potassium nitrate, with a minority of the synthetic resin adhesive and solvent, exploded 5 min after blending had started. Several possibilities of a frictional initiation source were considered.

Calcium hydroxide, Polychlorinated phenols
See Calcium hydroxide: Polychlorinated phenols, etc.

Calcium silicide
1. Berger, F., *Compt. rend.*, 1920, **170**, 1492
2. Smolin, A. O., *Chem. Abs.*, 1977, **86**, 173758

A mixture of potassium nitrate (or sodium nitrate) and calcium silicide (60:40) is a readily ignited primer which burns at a very high temperature. It is capable of initiating many high-temperature reactions [1]. The topic has been discussed subsequently but no details were translated [2].

Cellulose
Ishida, H. *et al., Chem. Abs.*, 1988, **109**, 56797
Thermal reaction hazards of potassium nitrate—cellulose mixtures were evaluated by ARC. Stoicheiometric mixtures (zero oxygen balance) showed the lowest ignition temperatures.

Chromium nitride
Partington, 1967, 744
The nitride deflagrates with the molten nitrate.

Honey, Sulfur
Winfield, J. , *The Gunpowder Mills of Fernilee*, 20 (Private publ. by Author: 21 New Rd, Whaley Bridge, SK23 7JG, UK), 1996
An early Chinese manuscript warns that seething this mixture endangers the experimenter's beard. It is a probable precursor of gunpowder.

Lactose
See Lactose: Oxidants

Metal sulfides MRH Antimony trisulfide 2.30/37, titanium disulfide 3.42/26
1. Mellor, 1939, Vol. 9, 270, 524
2. Mellor, 1941, Vol. 3, 745; Vol. 7, 91, 274
3. Mellor, 1943, Vol. 11, 647
4. Pascal, 1963, Vol. 8.3, 404

Mixtures of potassium nitrate with antimony trisulfide [1], barium sulfide, calcium sulfide, germanium monosulfide or titanium disulfide all explode on heating [2]. The mixture with arsenic disulfide is detonable, and addition of sulfur gives a pyrotechnic composition [2]. Mixtures with molybdenum disulfide are also detonable [3]. Interaction with sulfides in molten mixtures is violent .

Metals MRH Aluminium 7.15/35, iron 1.55/53, magnesium 7.57/42, sodium 3.10/58

Mellor, 1941, Vol. 7, 20, 116, 261; 1939, Vol. 9, 382

Mixtures of potassium nitrate and powdered titanium, antimony or germanium explode on heating, and with zirconium at the fusion temperature of the mixture.

Non-metals MRH Carbon 3.26/13, Phosphorus (yellow) 3.14/27, sulfur 2.97/21

1. *MCA Case History No. 1334*
2. Mellor, 1946, Vol. 5, 16
3. Brede, U., *Chem. Abs.*, 1981, **94**, 86603
4. Leleu, *Cahiers*, 1980, (99), 278
5. Mellor, 1941, Vol. 2, 820, 825; 1963, Vol. 2, Suppl. 2.2, 1939
6. Mellor, 1940, Vol. 8, 788
7. Mellor, 1939, Vol. 9, 35

A pyrotechnic blend of a finely divided mixture with boron ignited and exploded when the aluminium container was dropped [1]; (the aluminium container also may have been involved). Boron is not attacked at below 400°C, but is at fusion temperature or at lower temperatures if decomposition products (nitrites) are present [2]. The mixture has also been evaluated as a propellant [3]. Contact of powdered carbon with the nitrate at 290°C causes vigorous combustion [4] and a mixture explodes on heating. Gunpowder is the oldest known explosive and contains potassium nitrate, charcoal and sulfur, the latter to reduce ignition temperature and to increase the speed of combustion [5]. Mixtures of white phosphorus and potassium nitrate explode on percussion, and a mixture with red phosphorus reacts vigorously on heating [6]. Mixtures of potassium nitrate with arsenic explode vigorously on ignition [7].

Organic materials MRH Aniline 3.51/13, acetone 3.47/15, ethanol 3.31/16, toluene 3.56/12

1. Smith, A. J., *Quart. Natl. Fire Prot. Assoc.*, 1930, **24**, 39—44
2. Unpublished information, 1979

Potassium nitrate in cloth sacks stowed next to baled peat moss became involved in a ship fire and caused rapid flame spread and explosions [1]. Heat transfer salt from a new supplier was added to a pilot plant reactor salt bath. Some 12 h after start of heating to melt the bath contents a muffled explosion occurred, attributed to presence of organic impurities in the new salt [2].

See Cellulose, above.

See Sodium nitrate: Jute, etc.

Other reactants

Yoshida, 1980, 192

MRH values calculated for 19 combinations with oxidisable materials are given.

Phosphides

Mellor, 1940, Vol. 8, 839, 845

Boron phosphide ignites in molten nitrates; mixtures of the nitrate with copper(II) phosphide explode on heating, and that with copper monophosphide explodes on impact.

Reducants

Mellor, 1941, Vol. 2, 820

Mixtures of potassium nitrate with sodium phosphinate and sodium thiosulfate are explosive, the former being rather powerful.

See other REDOX REACTIONS

Sodium acetate MRH 2.55/34

Pieters, 1957, 30

Mixtures may be explosive.

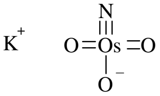
Thorium dicarbide

See Thorium dicarbide: Non-metals, etc.

See other METAL NITRATES, OXIDANTS

4646. Potassium nitridoosmate

[21774-03-8] **KNO_3Os**



$$K^+ \quad O{=}\overset{\overset{\displaystyle N}{|||}}{Os}{=}O \text{ with } Os{-}O^-$$

Clifford, A. F. *et al., Inorg. Synth.*, 1960, **6**, 205

Heating above 180°C at ambient pressure causes it to explode.

See related NITRIDES

4647. Potassium azide

[20762-60-1] **KN_3**

$$K^+ \quad \overset{-}{N}{=}\overset{+}{N}{=}N^-$$

Mellor, 1940, Vol. 8, 347

It is insensitive to shock; on heating progressively it melts, then decomposes evolving nitrogen, and the residue ignites with a feeble explosion.

Carbon disulfide

See Carbon disulfide: Metal azides

Manganese dioxide

See Manganese(IV)oxide: Potassium azide

Sulfur dioxide

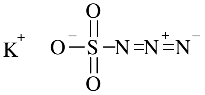
Mellor, 1940, Vol. 8, 347

Potassium azide explodes at 120°C when heated in liquid sulfur dioxide.

See other METAL AZIDES

4648. Potassium azidosulfate

[ ] **KN_3O_3S**



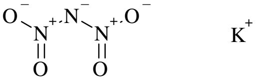
Mellor, 1940, Vol. 8, 314

It explodes on heating.

See other ACYL AZIDES

4649. Potassium dinitramide

[140456-79-7] **KN_3O_4**

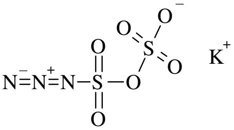


See Dinitramine

See other N—NITRO COMPOUNDS

4650. Potassium azidodisulfate

[67880-14-2] **KN_3O_6S**



Alone, or Water

Mellor, 1967, Vol. 8, Suppl. 2.2, 36

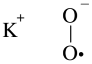
On keeping or slow heating, the salt produces explosive disulfuryl azide, and the salt reacts explosively with water.

See Sulfuryl diazide

See other ACYL AZIDES

4651. Potassium dioxide (Potassium superoxide)

[12030-88-5] **KO_2**



1. *Alkali Metals*, 1957, 174
2. Gilbert, H. N., *Chem. Eng. News*, 1948, **26**, 2604
3. Madaus, private comm., 1976
4. Kirk-Othmer, 1968, Vol. 16, 365—366

5. Commander, J. C., *ERDA Rep. ANCR 1217; TID-4500*, Springfield (Va.), USNTIS, 1975
6. Sloan, S. A., *Proc. Int. Conf. Liquid Met. Technol.*, Champion (Pa.), Int. At. En. Auth., 1976

The earlier references, which state that this powerful oxidant is stable when pure, but explosive when formed as a layer on metallic potassium [1,2], are not wholly correct [3], because the superoxide is manufactured uneventfully by spraying the molten metal into air to effect oxidation [4]. Previous incidents appear to have involved the explosive oxidation of unsuspected traces of mineral oil or solvents [3]. However, mixtures of the superoxide with liquid or solid potassium—sodium alloys will ignite spontaneously after an induction period of 18 min, but combustion while violent is not explosive [3]. The additional presence of water (which reduces the induction period) or hydrocarbon contaminant did produce explosion hazards under various circumstances [5]. Contact of liquid potassium with the superoxide gives no obvious reaction below 117°C and a controlled reaction between 117 and 177°C, but an explosive reaction occurs above 177°C. Heating at 100°C/min from 77° caused explosion at 208°C [6].

See Dipotassium *grkm*-cyclooctatetraene

See Potassium:- *Slow oxidation*

See other INDUCTION PERIOD INCIDENTS

2-Aminophenol, Tetrahydrofuran

1. Crank, G. *et al., Aust. J. Chem.*, 1984, **37**, 845—855
2. Crank, G. *et al., Chem. Eng. News*, 1988, **68**(35), 2

2-Aminophenol was being oxidised in THF solution at 65°C using a larger than normal proportion of potassium dioxide. When stirring was stopped after 6 h, a violent explosion occurred. This was attributed to formation of tetrahydrofuranyl hydroperoxide by the excess dioxide. THF was described as an unsafe solvent for superoxide reactions [1]. A later attempt at the same reaction in toluene also led to explosion, now blamed on the substrate [2].

See Hydrocarbons, below.

Carbon

Mellor, D. P., *Chem. & Ind.*, 1965, 723

Residues from extinguishing small sodium—potassium alloy fires with graphite were accumulated in an airtight drum. Later, burning alloy fell into the drum and caused a violent explosion. This was attributed to formation of potassium superoxide during storage, and explosive reaction of the latter with graphite, initiated by the burning alloy. Graphite is not a suitable extinguishant for fires involving potassium or its alloys.

Diselenium dichloride

Mellor, 1947, Vol. 10, 897

Interaction is very violent.

Ethanol

Health & Safety Inf., 251, Washington, USAEC, 1967

Disposal of a piece of potassium—sodium alloy under argon in a glove box by addition of ethanol caused violent gas evolution which burnt a glove and produced a flame. A piece of highly oxidised potassium exploded when dropped into ethanol. Both incidents were attributed to violent interaction of potassium superoxide and ethanol.

Hydrocarbons

Health & Safety Inf., 251, Washington, USAEC, 1967

Residues of potassium—sodium alloy in metal containers were covered with oil prior to later disposal. When a lid was removed later, a violent explosion occurred. This was attributed to frictional initiation of the mixture of potassium superoxide (formed on long standing of the alloy) and oil.

Metals

Mellor, 1941, Vol. 2, 493

Oxidation of arsenic, antimony, copper, potassium, tin or zinc proceeds with incandescence.

See reference 6 above

Organic compounds

Frimer, A. A. *et al., Photochem. Photobiol.*, 1978, **28**(4-5. Singlet oxygen), 718

Potassium superoxide must not be added to neat oxidation substrates, or ignition may occur, and weighing it out on filter paper is also hazardous.

Potassium—sodium alloy

Sloan, S. A. *et al., Microscope*, 1977, **25**, 237—243

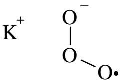
A runaway self heating reaction occurs 3.8 s after mixing at 201°C or above, and at that temperature an exotherm to 304°C at a rate above 2000°/s was observed, but no pressure effects were seen.

See other METAL OXIDES, OXIDANTS

See related METAL PEROXIDES

4652. Potassium trioxide (Potassium ozonide)

[12030-89-6] **KO_3**



See Caesium trioxide

See also Fluorine: Potassium hydroxide

See other METAL OXIDES

See related METAL PEROXIDES

4653. Potassium silicide

[16789-24-5] **KSi**

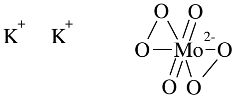
K—Si

Bailar, 1973, Vol. 1, 1357

It ignites in air.

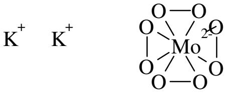
See other METAL NON-METALLIDES

4654. Potassium diperoxomolybdate
[58412-05-8] **K_2MoO_6**



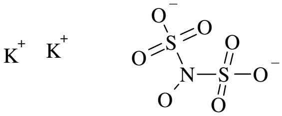
Mellor, 1943, Vol. 11, 607
It explodes on grinding.
See other PEROXOACID SALTS

4655. Potassium tetraperoxomolybdate
[56094-15-6] **K_2MoO_8**



Jahr, K. F., *FIAT Rev. Ger. Sci: Inorg. Chem., Pt. III*, 1948. 170
It is explosive.
See other PEROXOACID SALTS

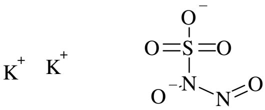
4656. Potassium nitrosodisulfate
[14293-70-0] **$K_2NO_7S_2$**



1. Zimmer, H. *et al., Chem. Rev.*, 1971, **71**, 230, 243
2. Wehrli, P. A. *et al., Org. Synth.*, 1972, **52**, 86

The observed instability of the solid radical on storage, ranging from slow decomposition to violent explosion (probably depending on the degree of confinement), depends largely upon the degree of contamination by nitrite ion. Storage conditions to enhance stability are detailed [1]. Synthetic use of solutions of the salt has been preferred, and the storage of any isolated salt as an alkaline slurry is recommended [2].
See related NITROSO COMPOUNDS

4657. Potassium *N*-nitrosohydroxylamine-*N*-sulfonate ('Potassium dinitrososulfite')
[26241-10-1] **$K_2N_2O_5S$**



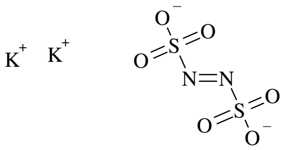
Weitz, E. *et al., Ber.*, 1933, **66**, 1718

The salt (formerly named a dinitrososulfite) explodes on heating.

See other N—O COMPOUNDS, N—S COMPOUNDS

4658. Potassium azodisulfonate

[ ] **$K_2N_2O_6S_2$**



Alone, or Water

Konrad, E. *et al., Ber.*, 1926, **59**, 135

There is a possibility of explosion during vacuum desiccation of the salt, which evolves nitrogen violently in contact with water.

See other N—S COMPOUNDS

See related AZO COMPOUNDS

4659. Potassium sulfurdiimidate

[79796-14-8] (ion) **K_2N_2S**

Alone, or Solvents, or Water

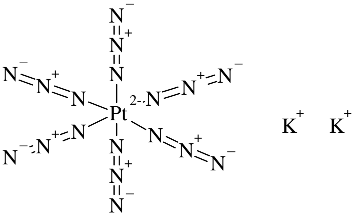
1. Goehring, 1957, 39, 6
2. Hornemann, K. *et al., Angew. Chem. (Intern. Ed.)*, 1982, **21**, 633

It ignites in air, and reacts violently and may explode with traces of water [1]. It is stable up to 180°C, but reacts explosively and ignites with water, methanol or chloromethane, methylene chloride or carbon tetrachloride [2].

See other N-METAL DERIVATIVES, N—S COMPOUNDS

4660. Potassium hexaazidoplatinate(IV)

[41909-62-0] (ion) **$K_2N_{18}Pt_2$**

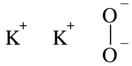


Mellor, 1940, Vol. 8, 355

Evaporation of a solution of hexachloroplatinic acid with a deficiency of potassium azide, or with an equivalence of ammonium azide gives explosive residues.

Evaporation of a solution of the acid with an equivalence (8 mol) of potassium azide leads to explosion of the conc. solution of the title compound.
See other PLATINUM COMPOUNDS
See related METAL AZIDES

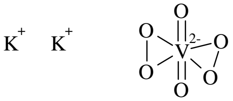
4661. Potassium peroxide
[17014-71-0] **K_2O_2**



Other reactants
Yoshida, 1980, 83
MRH values calculated for 15 combinations with oxidisable materials are given.

Water
Pascal, 1963, Vol. 2.2, 59
Interaction is violent or explosive.
See other METAL PEROXIDES, OXIDANTS

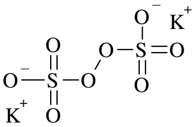
4662. Potassium diperoxoorthovanadate
[ ] **K_2O_6V**



1. Mellor, 1939, Vol. 9, 795
2. Emeléus, 1960, 425

It explodes on heating [1,2].
See other PEROXOACID SALTS

4663. Potassium peroxodisulfate
[7727-21-1] **$K_2O_8S_2$**



FPA H106, 1981; *HCS 1980*, 775

Energy of decomposition (in range 190—840°C) measured as 0.29 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Alkali, Hydrazine salts
Mellor, 1947, Vol. 10, 466

Addition of alkali to the mixed salts liberates hydrazine which is vigorously oxidised to nitrogen gas.

Potassium hydroxide

Anon., *BCISC Quart. Safety Summ.*, 1965, **36**, 41

Surface contamination of 2 kg of the dry salt with as little as 2 flakes of moist potassium hydroxide caused a vigorous self-sustaining fire, which was extinguished with water, but not by carbon dioxide or dry powder extinguishers.

Water

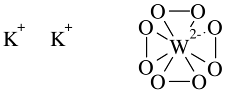
Castrantas, 1965

The salt rapidly liberates oxygen above 100°C when dry, but at only 50°C when wet.

See other OXIDANTS, PEROXOACID SALTS

4664. Potassium tetraperoxotungstate

[37346-96-6] **K_2O_8W**



Mellor, 1943, Vol. 11, 836

It explodes on friction or rapid heating to 80°C.

See other PEROXOACID SALTS

4665. Potassium sulfide

[1312-73-8] **K_2S**

$K^+ \quad K^+ \qquad S^{2-}$

HCS 1980, 387

Merck Index, 1983, p1104

The anhydrous sulfide is unstable, and may explode on percussion or rapid heating.

Chloroform: Ethanol (or Methanol)

See Potassium dithioformate

Nitrogen oxide

See Nitrogen oxide: Potassium sulfide

Other reactants

Yoshida, 1980, 83

MRH values calculated for 13 combinations with various reagents are given.

See other METAL SULFIDES

4666. Potassium nitride

[29285-24-3] **K_3N**

$K^+ \quad K^+ \quad K^+ \qquad N^{3-}$

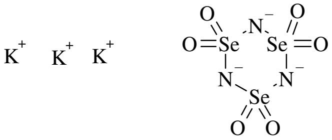
Mellor, 1940, Vol. 8, 99
It usually ignites in air.

Phosphorus
See Phosphorus: Potassium nitride

Sulfur
See Sulfur: Potassium nitride
See other NITRIDES

4667. Potassium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide ('Potassium triselenimidate')

[51593-99-8] **$K_3N_3O_6Se_3$**



Explosive.
See Selenium difluoride dioxide: Ammonia
See other N-METAL DERIVATIVES

4668. Potassium antimonide

[16823-94-2] **K_3Sb**

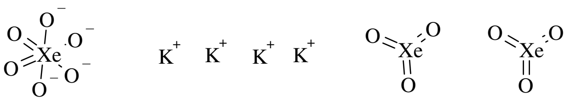
$K^+ \quad K^+ \quad K^+ \qquad Sb^{3-}$

1. Mellor, 1939, Vol. 9, 403
2. Rüst, 1948, 342

It usually ignites when broken in air [1] and explodes on exposure to moisture (in breath) [2].
See other ALLOYS, PYROPHORIC MATERIALS

4669. Potassium hexaoxoxenonate—xenon trioxide

[12273-50-6] **$K_4O_6Xe.2O_3Xe$**



1. Grosse, A. V., *Chem. Eng. News*, 1964, **42**(29), 42
2. Spittler, T. M. *et al., J. Amer. Chem. Soc.*, 1966, **88**, 2942
3. Appelman, E. H. *et al., J. Amer. Chem. Soc.*, 1964, **86**, 2141

The complex salt is very sensitive to mechanical shock and explodes violently [1,2], even when wet [3].
See other XENON COMPOUNDS
See related NON-METAL OXIDES

4670. Lithium tripotassium tetrasilicide

[102210-64-0] **K_3LiSi_4**

LiK_3Si_4

von Schering, H. G. *et al., Angew. Chem. (Intern. Ed.)*, 1986, **25**, 566
It ignites in air.
See other METAL NON-METALLIDES

4671. Lithium heptapotassium di(tetrasilicide)

[102210-65-1] **K_7LiSi_8**

$LiK_7(Si_4)_2$

von Schering, H. G. *et al., Angew. Chem. (Intern. Ed.)*, 1986, **25**, 566
It ignites in air.
See other METAL NON-METALLIDES

4672. Lanthanum

[7439-91-0] **La**

La

Nitric acid
Mellor, 1946, Vol. 5, 603
Oxidation is violent.

Phosphorus
See Phosphorus: Metals
See other METALS

4673. Lanthanum—nickel alloy

[12196-72-4] **$LaNi_5$**

La—Ni—Ni—Ni—Ni—Ni

Hydrogen
See Lanthanum pentanickel hexahydride

Hydrogen, Poly(tetrafluoroethylene)
See Poly(tetrafluoroethylene): Metal hydrides
See LANTHANIDE—TRANSITION METAL ALLOY HYDRIDES
See other ALLOYS, HYDROGENATION CATALYSTS

4674. Lanthanum oxide
[1312-81-8] **La_2O_3**

$$O{=}La{-}O{-}La{=}O$$

Chlorine trifluoride
See Chlorine trifluoride: Metals, etc.

Water
Sidgwick, 1950, 441
Interaction is vigorously exothermic, accompanied by hissing, as for calcium oxide.
See Calcium oxide: Water
See other METAL OXIDES

4675. Lithium
[7439-93-2] **Li**

Li

NSC 566, 1978; *HCS 1980*, 592

1. Mellor, 1941, Vol. 2, 468: 1961, Vol. 2, Suppl. 2.1, 71
2. *Haz. Chem. Data*, 1975, 187
3. Bullock, A., *Chem. Brit.*, 1975, **11**, 115
4. Bullock, A., *School Sci. Rev.*, 1975, **57**(119), 311—314; private comm., 1975
5. Lloyd, W. H., and Emley, E. F., *Chem. Brit.*, 1975, **11**, 334
6. Ireland, R. E. *et al., Org. Synth.*, 1977, **56**, 47
7. Fritsch, *Proc. 1st Int. Symp. Prev. Occup. Risks Chem. Ind.*, 208—211, Heidelberg, ISSA, 1970

MRH Oxygen 19.95/54

Finely divided metal may ignite in air at ambient temperature and massive metal above the m.p., 180°C, especially if oxide or nitride is present. Since lithium will burn in oxygen, nitrogen or carbon dioxide, and when alight it will remove the combined oxygen in sand, sodium carbonate, etc., it is difficult to extinguish once alight [1]. (*Note the very high MRH value above.*) Molten lithium is extremely reactive and will attack concrete and refractory materials. Use of normal fire extinguishers (containing water, foam, carbon dioxide, halocarbons, dry powders) will either accelerate combustion or cause explosion. Powdered graphite, lithium chloride, potassium chloride or zirconium silicate are suitable extinguishants [2]. A well-tried and usually uneventful demonstration of atmospheric oxidation of molten lithium led to an explosion [3]. A high degree of correlation of incidence of explosions with high atmospheric humidity was demonstrated, with the intensity of explosion apparently directly related to the purity of the sample of metal [4]. Other possible factors were also identified [5]. While cleaning lithium wire by washing with hexane, the wire must be dried carefully with a paper towel. Too-vigorous rubbing will cause a fire [6].

Lithium blocks containing traces of nitride but which had been supplied under argon in sealed tins were cut into 1 cm strips and stored under air in closed tins overnight until used. Lithium containing some nitride reacts slowly with nitrogen at

ambient temperature to form more nitride, which autocatalyses the reaction which progressively accelerates and becomes exothermic. The strips of lithium reacted with the nitrogen of the air in the closed tins, causing a partial vacuum and an oxygen-enriched atmosphere. When the tins collapsed, the impact and/or compression of the oxygen-enriched atmosphere caused ignition and fierce burning of the lithium, which was very difficult to extinguish inside the crushed tins [7].
See Metal chlorides
See also Water, below

Acetonitrile, Sulfur dioxide
Ebner, W. B. *et al., Proc. 8th Power Sources Symp.*, 119—124, 1982
An ARC study of the thermal and pressure behaviour of actual electric batteries under various atypical conditions showed the major contributions to the exothermic behaviour as the reactions between lithium and acetonitrile, lithium and sulfur and the decomposition of lithium dithionite. The first reaction can generate enough heat to trigger other exothermic rections. The hazards associated with the various parameters are quantified.
See Sulfur dioxide, below

Bromine pentafluoride
See Bromine pentafluoride: Acids, etc.

Bromobenzene
Koch-Light Labs., Ltd., private comm., 1976
In a modified preparation of phenyllithium, bromobenzene was added to finely powdered lithium (rather than coarse particles) in ether. The reaction appeared to be proceeding normally, but after about 30 min it became very vigorous and accelerated to explosion. It was thought that the powdered metal may have been partially coated with oxide or nitride which abraded during stirring, exposing a lot of fresh metal surface on the powdered metal.
See Sodium: Halocarbons (reference 8)
See also Halocarbons, below

Carbon disulfide
See Carbon disulfide: Alkali metals

Carbon, Lithium tetrachloroaluminate, Sulfinyl chloride
Kilroy, W. P. *et al., J. Electrochem. Soc.*, 1981, **128**, 934—935
In electric battery systems, lithium is inert to the electrolyte components in absence of carbon, but in presence of over 10% of carbon (pre-mixed by grinding with the metal), contact with the electrolyte mixture leads to ignition or explosion.
See Sulfinyl chloride, below

Carbon, Sulfinyl chloride
James, S. D. *et al., J. Electrochem. Soc.*, 1983, **130**, 2037—2040
Pregrinding lithium with carbon leads to ignition on contact with sulfinyl chloride in electric battery systems. The effect of moisture and purity of the carbon on reactivity was studied.

Chlorine tri- or penta-fluorides
See Chlorine trifluoride: Metals, etc.

1-Chloro-3-dimethylaminopropane

1. Eisenbach, A. *et al., Euro. Polym. J.*, 1975, **11**, 699
2. Service, D., *Chem. Brit.*, 1987, **23**, 27
3. Bell, J. A. *et al., J. Org. Chem.*, 1959, **24**, 2036
4. Kamienskis, C. W., *Chem. Brit.*, 1987, **23**, 531—532

The preparation of 1-lithio-3-dimethylaminopropane according to a published procedure [1] involved reaction of the chloro compound with a mineral oil dispersion of lithium (30%) in hexane at 0°C. It had previously been found that lithium with a sodium content of some 0.3% reacted slowly, even at temperatures above 15°C. When a new batch of lithium (later found to contain 1.9% of sodium) was used, a vigorous reaction which set in at between 0° and —35°C led to ignition of the reaction mixture [2]. Although it was known that the presence of sodium increased the reactivity of lithium towards organohalides up to a sodium content of 2% [3], it had not been appreciated that such wide variations in reactivity were likely, or that a hazardous situation could develop [1,2]. However, a more likely cause proposed for the runaway exothermic reaction was the fact that all the reagents were mixed at 0°C, rather than the more usual course of adding the halide slowly to the lithium dispersion in a hydrocarbon solvent lower-boiling than hexane, so as to maintain gentle reflux at 35—50°C. Some general precautions for this type of reaction are given [4].
See Halocarbons, below

1,2-Diaminoethane, Tetralin
Reggel, A. *et al., J. Org. Chem.*, 1957, **22**, 892
Reduction of tetralin to octalin with lithium and ethylenediamine proceeds slowly, but if heated to 85°C it becomes violent, with rapid evolution of hydrogen.
See other GAS EVOLUTION INCIDENTS

Diazomethane
See Diazomethane: Alkali metals

Diborane MRH 1.13/99+
See Diborane: Metals

Ethylene
Pascal, 1966, Vol. 2.1, 38
Passage of the gas over heated lithium causes the latter to incandesce, producing a mixture of lithium hydride and lithium acetylide.
See Metal chlorides, etc., below

Halocarbons
MRH Bromoform 3.77/92, carbon tetrabromide 3.89/92, carbon tetrachloride 8.24/85, carbon tetraiodide 1.42/95, chloroform 7.78/85, fluorotrichloromethane 9.29/83, tetrachloroethylene 8.16/86

1. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
2. *Pot. Incid. Rep.*, 1968, **39**, ASESB, Washington
3. Pittwell, L. R., *J. R. Inst. Chem.*, 1959, **80**, 552

4. BDH Catalogue Safety Note, 969DD/14.0/0773, 1973
5. *491M*, 1975, 230

Mixtures of lithium shavings and several halocarbon derivatives are impact-sensitive and will explode, sometimes violently [1,2]. Such materials include: bromoform, carbon tetrabromide, carbon tetrachloride, carbon tetraiodide, chloroform, dichloromethane, diiodomethane, fluorotrichloromethane, tetrachloroethylene, trichloroethylene and 1,1,2-trichlorotrifluoroethane. In an operational incident, shearing samples off a lithium billet immersed in carbon tetrachloride caused an explosion and continuing combustion of the immersed metal [3]. Lithium which had been washed in carbon tetrachloride to remove traces of oil exploded when cut with a knife. Hexane is recommended as a suitable washing solvent [4]. A few drops of carbon tetrachloride on burning lithium was without effect, but a 25 cc portion caused a violent explosion [5].

See 1-Chloro-3-dimethylaminopropane, above
See Poly(1,1-difluoroethylene—hexafluoropropylene), below
See entry HALOCARBONS: METALS

Halogens MRH Chlorine 9.62/83

1. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
2. Mellor, 1961, Vol. 2, Suppl. 2.1, 82

Mixtures of lithium and bromine are unreactive unless subject to heavy impact, when explosion occurs [1]. Lithium and iodine react above 200°C with a large exotherm [2].

Hydrogen

See Hydrogen: Metals

Mercury

1. Smith, G. McP. *et al., J. Amer. Chem. Soc.*, 1909, **31**, 799
2. Alexander, J. *et al., J. Chem. Educ.*, 1970, **47**, 277

Interaction to form lithium amalgam is violently exothermic and may be explosive if large pieces of lithium are used [1]. An improved technique, using *p*-cymene as inerting diluent, is described in the later reference [2].

Metal chlorides, Nitrogen

Anon., *BCISC Quart. Safety Summ.*, 1969, **40**, 16

Accidental contamination of lithium strip with anhydrous chromium trichloride or zirconium tetrachloride caused it to ignite and burn vigorously in the nitrogen atmosphere of a glove box.

Metal oxides and chalcogenides MRH Chromium trioxide 7.20/83, sodium peroxide 13.64/71

1. Mellor, 1967, Vol. 2, Suppl. 2.1, 81—82
2. *Alkali Metals*, 1957, 11

Lithium is used to reduce metallic oxides in metallurgical operations, and the reactions, after initiation at moderate temperatures, are violently exothermic and rapid. Chromium(III) oxide reacts at 185°C, reaching 965°; similarly molybdenum trioxide (180 to 1400°), niobium pentoxide (320 to 490°), titanium dioxide (200—400 to 1400°), tungsten trioxide (200 to 1030°), vanadium pentoxide (394 to 768°); also iron(II) sulfide (260 to 945°), and manganese telluride (230 to 600°C) [1]. Residual mixtures from lithium production cells containing lithium and rust sometimes ignite when left as thin layers exposed to air [2].

Metals

1. Bailar, 1973, Vol. 1, 343—344
2. Popov, E. I. *et al., Chem. Abs.*, 1989, **110**, 100000

Formation of various intermetallic comounds of lithium by melting with aluminium, bismuth, calcium, lead, mercury, silicon, strontium, thallium or tin may be very vigorous and dangerous to effect [1]. Ignition and combustion hazards of alloys of lithium with aluminium or magnesium have been studied, the latter being more reactive than the former. Use of nitrogen as a protective medium for alloy powders is ineffective, mixed nitrides being formed [2].

See Mercury, above; Platinum, below

Nitric acid MRH 15.27/60

Accident & Fire Prev. Info., March, 1974, Washington, USAEC

Lithium ignited on contact with nitric acid and the reaction became violent, ejecting burning lithium.

Nitryl fluoride

See Nitryl fluoride: Metals

Non-metal oxides

Mellor, 1961, Vol. 2, Suppl. 2.1, 74, 84, 88

Although carbon dioxide reacts slowly with lithium at ambient temperature, the molten metal will burn vigorously in the gas, which cannot be used as an extinguisher on lithium fires. Carbon monoxide reacts in liquid ammonia to give the carbonyl which reacts explosively with water or air. Lithium rapidly attacks silica or glass at 250°C.

See Sulfur dioxide, below

See other GLASS INCIDENTS

Other reactants

Yoshida, 1980, 385—386

MRH values calculated for 24 combinations with various reducible materials are given.

Platinum

See Platinum: Lithium

Poly(1,1-difluoroethylene—hexafluoropropylene) (Viton)

Markowitz, M. M. *et al., Chem. Eng. News*, 1961, **39**(32), 4

Mixtures of finely divided metal and shredded polymer ignited in air on contact with water, or on heating to 369°C, or at 354° under argon.

See Halocarbons, above

Sodium carbonate, or Sodium chloride MRH Sodium carbonate 4.27/73

Mellor, 1961, Vol. 2, Suppl. 2.1, 25

Sodium carbonate and sodium chloride are unsuitable to use as extinguishers for lithium fires, since burning lithium will liberate the more reactive sodium in contact with them.

Sulfinyl chloride

1. Abraham, K. M. *et al., Proc. 28th Power Sources Symp.*, 1978, 255—257
2. Subbarao, S. *et al., Proc. Electrochem. Soc.*, 1988, **88-6**, 187—200
3. Ducatman, A. M. *et al., J. Occup. Med.*, 1988, **30**, 309—311
4. Butakov, A. A. *et al., J. Power Sources*, 1992, **39**(3), 375

An experimental investigation of explosion hazards in lithium—sulfinyl chloride cells on forced discharge showed cathode limited cells are safe, but anode limited cells may explode without warning signs [1]. Extended reversal at —40°C caused explosion on warming to ambient temperature, owing to thermal runaway caused by accelerated corrosion of lithium [2]. The violent explosion of a large prismatic cell of a battery is described [3]. Another study of explosion mechanisms in lithium/thionyl chloride batteries is reported [4].

See Carbon, etc., above

Sulfur

Mellor, 1961, Vol. 2, Suppl. 2.1, 75

Interaction when either is molten is very violent and, even in presence of inert diluent, the reaction begins explosively. Reaction of sulfur with lithium dissolved in liquid ammonia at —33°C is also very vigorous.

Sulfur dioxide

1. Dey, A. N. *et al., Chem. Abs.*, 1980, **93**, 10716, 10717
2. Crofts, C. C., *Chem. Abs.*, 1983, **99**, 56425
3. Subbarao, S. *et al., J. Power Sources*, 1987, **21**(3—4), 221—237
4. Donaldson, G. J., *et al., Power Sources*, 1991, **13**, 363

Two reports cover safety studies on lithium—sulfur dioxide batteries [1]. The cause of violent venting of discharged lithium—sulfur dioxide cells was ascribed to corrosion in a glass to metal seal and formation of lithium—aluminium alloys and other cathode reaction product(s) which are both shock-sensitive [2] The pyrophoric charged anodes of lithium—sulfur dioxide batteries are covered with smooth crystalline platelets, but partially discharged anodes are covered with a rough, non-adherent layer of lithium dithionite. The explosions which may occur during charging are attributed to thermal runaway reactions of lithium and sulfur dioxide to form lithium dithionite, LiOSO.SO.OLi [3]. A study of battery explosions consequent upon anode breakage in lithium—sulfur dioxide cells is reported [4].

See Acetonitrile, etc.

See also Non-metal oxides, above

Trifluoromethyl hypofluorite

See Trifluoromethyl hypofluorite: Lithium

Water.

1. Mellor, 1961, Vol. 2, Suppl. 2.1, 72
2. Bailar, 1973, Vol. 1, 337
3. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633—636
4. Usher, J. www.dne.bnl.gov/etd/csc/1997 (quarter 3)

Reaction with cold water is of moderate vigour, but violent with hot water, and the liberated hydrogen may ignite [1]. The powdered metal reacts explosively with water

[2]. The reactivity of lithium and other alkali metals with various forms of water has been discussed in detail. Prolonged contact with steam forms a thermally insulating layer which promotes overheating of the metal and may lead to a subsequent explosion as the insulating layer breaks up [3]. There is a report of a minor explosion and fire during washing of a reactor lid probably splashed with molten lithium during prior use [4].
See ALKALI METALS
See other METALS

4676. Lithium—magnesium alloy
[12384-02-0] **Li—Mg**

Li—Mg

Danyshova, T. A. *et al., Chem. Abs.*, 1982, **97**, 167510
Fire hazard (title only translated).
See other ALLOYS

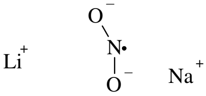
4677. Lithium—tin alloys
[12359-06-7] **Li—Sn**

Li—Sn

Alkali metals, 1957, 13

Lithium—tin alloys are pyrophoric.
See other ALLOYS, PYROPHORIC MATERIALS

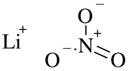
4678. Lithium sodium nitroxylate
[ ] **$LiNNaO_2$**



$Li^{+} \quad {}^{-}O-N^{\bullet}-O^{-} \quad Na^{+}$

Mellor, 1961, Vol. 2, Suppl. 2.1, 78
It decomposes violently at 130°C.
See other N—O COMPOUNDS

4679. Lithium nitrate
[7790-69-4] **$LiNO_3$**



$Li^{+} \quad {}^{-}O-N^{+}(-O^{-})=O$

Ethanol
See VAPOUR EXPLOSIONS (reference 3)

Other reactants

Yoshida, 1980, 208

MRH values calculated for 15 combinations with oxidisable materials are given.

Propene, Sulfur dioxide

See Propene: Lithium nitrate, etc.

See other METAL NITRATES

4680a. Lithium azide

[19597-69-4] **LiN_3**

$$\overset{+}{Li} \qquad \overset{-}{N}{=}\overset{+}{N}{=}N^{-}$$

Mellor, 1940, Vol. 8, 345

Insensitive to shock, the moist or dry salt decomposes explosively at 115—298°C, depending on the rate of heating.

Alkyl nitrates, Dimethylformamide

Polansky, O. E., *Angew. Chem. (Intern. Ed.)*, 1971, **10**, 412

Although these reaction mixtures are stable at 25°C during preparation of *tert*-alkyl azides, above 200°C the mixtures are shock-sensitive and highly explosive.

See other METAL AZIDES

4680b. Lithium ozonide

[ ] **LiO_3**

$$\overset{+}{Li} \qquad \overset{-}{O}{-}O{-}O\cdot$$

Korber, N. *et al., Chem. Ber.*, 1996, **129**(7), 773

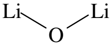
It was not possible to isolate this from liquid ammonia solution after formation by an exchange reaction with caesium ozonide. It was possible to isolate a cryptand complex, which was violently explosive but permitted diffraction studies. Sodium ozonide behaved similarly, though the other three alkali ozonides do not oxidise ammonia during isolation attempts.

See other METAL OXIDES

See related METAL PEROXIDES

4681. Lithium oxide

[12057-24-8] **Li_2O**



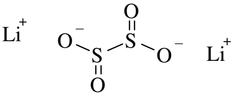
Metal halide hydrates

Rowley, A. T. *et al., Inorg. Chem. Acta,* 1993, **211**(1), 77

Preparation of metal oxides by fusing metal halides with lithium oxide in a sealed tube leads to explosions if halide hydrates are employed, particularly lanthanide trihalide

hydrates. The preparation succeeds with anhydrous halides. This will be purely a question of vapour pressure above an exothermic reaction; the question is whether the vapour is water, or metal halide, and the reaction oxide formation, or hydration of lithium oxide. Like other alkali metal oxides, hydration is extremely energetic.
See Diprotium monoxide

4682. Lithium dithionite
[59744-77-3] **$Li_2O_4S_2$**



See Lithium: Sulfur dioxide (reference 3)
See other METAL OXONON-METALLATES, REDUCANTS

4683. Lithium nitride
[26134-62-3] **Li_3N**

Li^+ Li^+ Li^+ N^{3-}

Air, or Water

1. 'Data Sheet TD 121', Exton, Foote Mineral Co., 1965
2. Schönher, E. *et al., Inorg. Synth.*, 1983, **22**, 48—55

The finely divided powder may ignite if sprayed into moist air [1]. Procedures for preparing polycrystalline and single crystal materials are detailed, with precautions to prevent ignition of material deposited on the walls of the reaction chamber when it is opened to air, or cleaned with water [2].

Copper(I) chloride
Mellor, 1940, Vol. 8, 100
Heated interaction to produce metallic copper is violent.

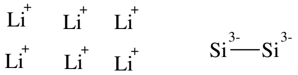
Silicon tetrafluoride
Porritt, L. J., *Chem. Brit.*, 1979, **15**, 282—283
Interaction is violently exothermic, causing sealed glass tubes at 350°C to explode, and a flow reaction system partially to melt.
See other GLASS INCIDENTS

Transition metal halides
Hector, A. *et al., J. Chem. Soc., Chem. Comm.*, 1993, (13), 1095; *J. Chem. Soc., Dalton Trans.*, 1993, (16), 2435
Titanium and vanadium nitrides may be prepared by a metathesis reaction of their tetrachlorides with the nitride, initiated by heat or friction. The reaction is potentially explosive. Other transition metal halides may cause ampules to explode after thermal initiation when anhydrous and were invariably found to do so when the hydrates were used.

See METAL PNICTIDES, METATHESIS
See other NITRIDES

4684. Hexalithium disilicide

[12136-61-7] **Li_6Si_2**



Acids

Mellor, 1940, Vol. 6, 170

The silicide incandesces in conc. hydrochloric acid, and with dilute acid evolves silanes which ignite. It explodes with nitric acid and incandesces when floated on sulfuric acid.

Halogens

Mellor, 1940, Vol. 6, 169

When warmed, it ignites in fluorine, but higher temperatures are necessary with chlorine, bromine and iodine.

Non-metals

Mellor, 1940, Vol. 6, 169

Interaction with phosphorus, selenium or tellurium causes incandescence. Sulfur also reacts vigorously.

Water

Mellor, 1940, Vol. 6, 170

Reaction with water is very violent, and the silanes evolved ignite.

See other METAL NON-METALLIDES

4685. Magnesium

[7439-95-4] **Mg**

Mg

NSC 426, 1981; *FPA H21*, 1974 (not powder); *HCS 1980*, 598

1. *Dust Explosion Prevention: Magnesium Powder, NFPA Standard Codes 480, 651*, both 1987
2. Popov, E. I., *Chem. Abs.*, 1975, **82**, 61415
3. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
4. www.chemsafety. gov/circ. US Chem. Safety & Haz. Investigation Board, CSB 2001-5271; 2001-5283; 2002-5521
5. Dang, J. *et al., Chem. Abs.*, 2003, **141**, 353331a

All aspects of prevention of magnesium (and aluminium) dust explosions in storage, handling or processing operations are covered in two US National Fire Codes [1]. Effects of various parameters on ignition of magnesium powders were studied [2]. Maximum explosion pressures of 7.9 bar, with maximum rate of rise of 884 bar/s have been recorded [3,5]. Magnesium powder and flake may ignite in storage, usually after contact with water, especially the residue left after extinction of a previous fire [4].

Acetylenic compounds
See ACETYLENIC COMPOUNDS: Metals

Aluminium, Rusted steel, Zinc
See Aluminium—magnesium—zinc alloy: Rusted steel

Ammonium salts, Chlorate salts MRH Ammonium chlorate 9.07/74
Kirk-Othmer (3rd ed.), 1982, Vol. 19, 494
The mixture ignites when wet owing to formation of unstable ammonium chlorate, and combustion of the metal is very intense.

Atmospheric gases, Water
Darras, R. *et al., Chem. Abs.*, 1961, **55**, 13235
The temperature at which massive magnesium and its alloys will ignite in air depends on the heating programme and the presence or absence of moisture.

Barium carbonate, Water
MCA Case History No. 1849
Fusion of the metal and salt formed barium acetylide, to which water was added without effective cooling. The vigorous evolution of acetylene blew off the reactor lid and the hot acetylene ignited in air.
See other GAS EVOLUTION INCIDENTS

Beryllium fluoride
Walker, H. L., *School Sci. Rev.*, 1954, **35**(127), 348
Interaction is violently exothermic.

Boron diiodophosphide
See Boron diiodophosphide: Metals

Calcium carbonate, Hydrogen
Mellor, 1940, Vol. 4, 271
Heating an intimate mixture of the powdered metal and carbonate in a stream of hydrogen leads to a violent explosion.

Carbon dioxide MRH 8.66/49

1. Partington, 1967, 475
2. Driscoll, J. A., *J. Chem. Educ.*, 1978, **55**, 450—451
3. Darras, R. *et al., Chem. Abs.*, 1961, **55**, 13235

A mixture of solid carbon dioxide and magnesium burns very rapidly and brilliantly when ignited [1]. Details for a safe demonstration of the violent combustion have been published [2]. The temperature at which massive magnesium and its alloys will ignite carbon dioxide at 1 bar or 15 bar pressure depends on the heating programme and the presence or absence of moisture. Steady progressive heating caused ignition in carbon dioxide at 900°C (780° if moist), or at 800°C after 4 h (650°/40 min if moist), combustion being violent [3].

Carbon tetrachloride, MRH 5.65/76
See Methanol: Carbon tetrachloride, Metals

Chloroformamidinium nitrate
See Chloroformamidinium nitrate: Metals

Copper compounds
Gorbunov, V. V. *et al., Combustion, Expls, & Shockwaves*, 1986, **22**, 726
Not merely cupric oxide, but the fluoride, chloride and sulfide all form mixtures with heats of combustion above 2kJ/g. The equivalent lead compounds are less active.

Ethylene oxide MRH 6.82/79
See Ethylene oxide (reference 3)

Fluorocarbon polymers
Kirk-Othmer (3rd ed.), 1982, Vol. 19, 495
Compressed mixtures are used as special igniters.
See Halocarbons, below

Glass powders
See Metal oxides, below (reference 3)

Halocarbons MRH Carbon tetrachloride 5.65/76, trichloroethylene 5.48/78

1. Clogston, C. C., *Bull. Res. Underwriters Lab.*, 1945, **34**, 5
2. *Pot. Incid. Rept.*, 39, ASESB, Washington, 1968
3. Mond. Div. ICI, private comm., 1968
4. Hartmann, I., *Ind. Eng. Chem.*, 1948, **40**, 756
5. *Haz. Chem. Data.*, 1975, 115

The powdered metal reacts vigorously and may explode on contact with chloromethane, chloroform, or carbon tetrachloride, or mixtures of these [1]. Mixtures of powdered metal with carbon tetrachloride or trichloroethylene will flash on heavy impact [2]. Violent decomposition with evolution of hydrogen chloride can occur when 1,1,1-trichloroethane comes into contact with magnesium or its alloys with aluminium [3]. Magnesium dust ignited at 400°C in dichlorodifluoromethane (used as an extinguishant for hydrocarbon fires) and suspensions of the dust exploded violently on sparking in the vapour [4]. Interaction with 1,2-dibromoethane may become violent, and gives air-sensitive Grignard compounds [5].
See Bromomethane: Metals
See Fluorocarbon polymers, above; Polytetrafluoroethylene, below
See other CORROSION INCIDENTS

Halogens, or Interhalogens MRH Chlorine 6.78/75, fluorine 17.78/61
Mellor, 1940, Vol. 4, 267
It ignites if moist and burns violently in fluorine, and ignites in moist or warm chlorine. It burns not very readily in bromine vapour and may ignite if finely divided on heating in iodine vapour.
See Chlorine trifluoride: Metals
    Iodine heptafluoride: Metals
    Iodine: Metals, Water

Hydrogen iodide

Mellor, 1941, Vol. 2, 206

Contact causes momentary ignition.

Lead compounds

See Copper compounds, above

Magnesium sulfate

See Magnesium sulfate: Magnesium

Metal cyanides

Mellor, 1940, Vol. 4, 271

Magnesium reacts with incandescence on heating with cadmium cyanide, cobalt cyanide, copper cyanide, lead cyanide, nickel cyanide and zinc cyanide. With gold cyanide or mercury cyanide, the cyanogen released by thermal decomposition of these salts reacts explosively with magnesium.

Metal oxides MRH Chromium trioxide 6.44/73, lead dioxide 3.22/83

1. Mellor, 1941, Vol. 3, 138, 378; 1940, Vol. 4, 272; 1941, Vol. 7, 401
2. Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64
3. Lawrence, K. D. *et al., Chem. Abs.*, 1979, **91**, 41576

Magnesium will reduce violently metal oxides on heating, similarly to aluminium powder in the thermite reaction. Beryllium oxide, cadmium oxide, copper oxide, mercury oxide, molybdenum oxide, tin oxide and zinc oxide are all reduced explosively on heating. Silver oxide reacts with explosive violence when heated with magnesium powder in a sealed tube [1]. Interaction of molten magnesium and iron oxide scale is violent [2]. Use of glass powders as suppressants for burning magnesium showed that some lithium oxide—magnesium oxide frits reacted violently [3].

See other GLASS INCIDENTS, THERMITE REACTIONS

Metal oxosalts

MRH Ammonium nitrate 8.79/69, potassium nitrate 7.57/58, silver nitrate 6.95/70, barium sulfate 4.27/71, copper(II) sulfate 7.03/58, sodium sulfate 5.86/60, potassium carbonate, 3.10/66.

1. Mellor, 1940, Vol. 4, 272; Vol. 8, Suppl. 2.1, 545
2. Pieters, 1957, 30
3. Shimizu, T., *Chem. Abs.*, 1991, **114**, 9175

Interaction with fused ammonium nitrate or with metal nitrates, phosphates or sulfates may be explosively violent [1]. Lithium and sodium carbonates may also react vigorously [2]. The mixture with magnesium sulfate has been described as a noisy but low power bursting charge for pyrotechny [3].

See Silver nitrate: Magnesium

  Potassium perchlorate: Metal powders

See other THERMITE REACTIONS

Methanol MRH 5.02/73

1. Vogel, 1957, 169
2. Personal experience, 1952
3. Shidlovskii, A. A., *Chem Abs.*, 1947, **41**, 1105d

The reaction of magnesium and methanol to form magnesium methoxide and used to prepare dry methanol [1] is very vigorous, but often subject to a lengthy induction period. Sufficient methanol must be present to absorb the violent exotherm which sometimes occurs [2]. Mixtures of powdered magnesium (or aluminium) and methanol are capable of detonation and are more powerful than military explosives [3].
See other INDUCTION PERIOD INCIDENTS

Methanol, 3-Methyl-2-butenoylanilide
Brettle, R. *et al., Tetrahedron Lett.*, 1980, **21**, 2915
Reduction of the double bond in the anilide by magnesium in methanol is vigorously exothermic after an induction period, and efficient cooling is then necessary.
See Methanol, above.
See other INDUCTION PERIOD INCIDENTS

Molybdenum disulfide
See Molybdenum disulfide, Magnesium

Nitric acid, 2-Nitroaniline
See Nitric acid: Magnesium, 2-Nitroaniline

Nitrogen
See Nitrogen (Liquid): Magnesium

Other reactants
Yoshida, 1980, 347—348
MRH values calculated for 31 combinations, largely with oxidants, are given.

Oxidants	MRH values show % of oxidant
See Carbon dioxide, above	
Ammonium nitrate: Metals	MRH 8.79/69
Barium peroxide: Metals	
Dinitrogen tetraoxide: Metals	MRH 12.97/50
Hydrogen peroxide: Metals	MRH 12.68/59
Lead(IV)oxide: Metals	MRH 3.22/83
Nitric acid: Metals	MRH 11.97/52
Oxygen (Liquid): Metals	
Potassium chlorate: Metals	MRH 9.50/63
Potassium perchlorate: Powdered metals	
Sodium iodate: Metals	
Sodium nitrate: Magnesium	MRH 8.58/58
See Halogens etc., above	
See Metal oxides, above	
See Metal oxosalts, above	
See Sulfur, etc., below	

Poly(tetrafluoroethylene)

1. Anon., *Indust. Res.*, 1969(9), 15
2. Diercks, B. V., *J. Haz. Mat.*, 1986, **12**(1), 3
3. Potter, L. J., *Proc. 13th Int. Pyrotech. Semin.*, 1988, 639—659

Finely divided magnesium and Teflon are described as a hazardous combination of materials [1]. The compressed pellets of powdered metal and polymer used as infrared decoy flares have been found sensitive to ignition by electrostatic sparks during manufacture [2]. The ignition sensitivity of igniter mixtures containing magnesium, Teflon and Viton was studied, following two fires [3].
See Fluoropolymers
See also Halocarbons, above

Potassium carbonate MRH 3.10/66
Winckler, C., *Ber.*, 1890, **23**, 442
The mixture of magnesium and potassium carbonate recommended by Castellana as a safe substitute for molten sodium in the Lassaigne test can itself be hazardous, as an equimolar mixture gives an explosive substance (possibly 'carbonylpotassium', potassium benzenehexoxide) on heating.

Rusty steel
Billinge, K., *Fire Prev. Sci. Technol.*, 1981, (24), 13—19
Impact of a magnesium anode on rusty steel led to ignition and explosion in a tanker.
See other THERMITE REACTIONS

Silicon dioxide
1. Barker, W. D., *School Sci. Rev.*, 1938, **20**(77), 150
2. Marle, E. R., *Nature*, 1909, **82**, 428

Heating a mixture of powdered magnesium and silica (later found not to be absolutely dry) caused a violent explosion rather than the vigorous reaction anticipated [1]. A warning had been published previously [2].
See also FLASH POWDER

Sulfur, or Tellurium MRH Sulfur 6.15/57
1. Brauer, 1963, Vol. 1. 913
2. Hutton, K., *School Sci. Rev.*, 1950, **31**(114), 265
3. Bodner, G. M., *J. Chem. Educ.*, 1985, **62**(12), 1107

Interaction of magnesium with sulfur or tellurium at elevated temperatures may be violent [1] or even explosive [2], even with tiny amounts [3].
See Sulfur: Metals

Water
1. Shidlovskii, A. A., *Chem. Abs.*, 1947, **41**, 1105d
2. Taylor, F. R. *et al., Rept. ARAED-T-87022*, 1—26, 1988; O/no. AD A187158, NTIS, Richmond (Va.)

Mixtures of magnesium (or aluminium) powder with water can be caused to explode powerfully by initiation with a boosted detonator [1]. The use of organic coatings on magnesium or aluminium powder in pyrotechnic compositions prevents reaction with atmospheric moisture and problems resulting from hydrogen evolution [2].
See Methanol, above
See also Aluminium—magnesium alloy: Water

Water, Uranium

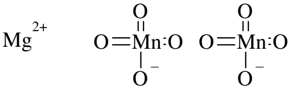
1. Anon., *Loss Prev. Bull.*, 1992, **103**, 19
2. Pitt, M. J., personal communication, 1993
3. USA DOE, Office of Nuclear Safety, Safety Notice 97-01, 1997

A drum of graphite with magnesium and uranium, stored underwater with a 6mm diameter relief hole, burst and scattered its contents. This was attrributed to insufficient venting of hydrogen evolved by reaction of magnesium and water [1]. A similar, but larger scale, event is also attributed to magnesium but holds that this was activated by prior reaction between water and metallic uranium [3]. If the uranium was present as metal, it seems likely to have been an even more potent source of hydrogen [2].

See other CORROSION INCIDENTS, METALS, REDUCANTS

4686. Magnesium permanganate

[10377-62-5] **$MgMn_2O_8$**



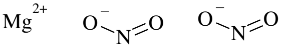
Organic compounds

See Zinc permanganate: Organic compounds

See other METAL OXOMETALLATES, OXIDANTS

4687. Magnesium nitrite

[15070-34-5] **MgN_2O_4**



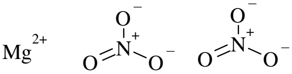
Ephraim, 1939, 686—687

Less stable, more hygroscopic and readily hydrolysed than alkali metal nitrites, it may function as a more powerful oxidant.

See other METAL NITRITES, OXIDANTS

4688. Magnesium nitrate

[10377-60-3] **MgN_2O_6**



HCS 1980, 601

Dimethylformamide MRH 5.06/22

'DMF Brochure', Billingham, ICI Ltd., 1965

Magnesium nitrate has been reported to undergo spontaneous decomposition in DMF, (possibly as a result of hydrolysis of the hexahydrate above its m.p., 90°C to liberate

nitric acid). Although this effect has not been observed with other nitrates, reaction mixtures with hydrolysable nitrates should be treated with care.
See Sodium nitrate: Jute, Magnesium chloride

Other reactants
Yoshida, 1980, 205
MRH values calculated for 16 combinations with oxidisable materials are given.

Tin(II) fluoride
Denes, G., *Chem. Eng. News*, 1988, **66**(14), 2
Addition of an aqueous solution of the fluoride to one of the nitrate unexpectedly gave no precipitate of magnesium fluoride, and the solution was allowed to evaporate, first at ambient temperature, and then in a warm place, giving a wet white solid. While being manipulated with a spatula, this exploded with some violence, brown fumes were evolved and the solid was transformed into a dry tan-coloured powder. It was thought that oxidation of tin(II) to (IV) had occurred, the nitrate being reduced to nitrogen oxide.
See Tetrahydroxotritin(2+) nitrate
See other METAL NITRATES, OXIDANTS, REDOX REACTIONS

4689. Magnesium azide
[39108-12-8] **MgN_6**

$$\overset{-}{N}=\overset{+}{N}=N^{-} \quad Mg^{2+} \quad \overset{-}{N}=\overset{+}{N}=N^{-}$$

Mellor, 1940, Vol. 8, 350
It explodes on heating.
See other METAL AZIDES

4690. Magnesium oxide
[1309-48-4] **MgO**

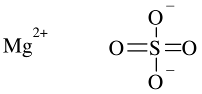
$$Mg^{2+} \qquad O^{2-}$$

HCS 1980, 602

Interhalogens
See Bromine pentafluoride: Acids, etc., Chlorine trifluoride: Metals, etc.

Phosphorus pentachloride
See Phosphorus pentachloride: Magnesium oxide
See other INORGANIC BASES, METAL OXIDES

4691. Magnesium sulfate
[18939-43-0] **MgO_4S**



$$Mg^{2+} \qquad O=\overset{\overset{\large O^-}{|}}{\underset{\underset{\large O^-}{|}}{S}}=O$$

HCS 1980, 603

Ethoxyethynyl alcohols

See ETHOXYETHYNYL ALCOHOLS

See other METAL OXONON-METALLATES

Magnesium

Shimizu, T., *Chem. Abs.*, 1991, **114**, 9175

The mixture with magnesium powder has been described as a pyrotechnic explosive.

See Magnesium: Metal oxosalts

4692. Magnesium silicide

[22831-39-6] **Mg_2Si**

Mg_2Si

Acids, Water

Sorbe, 1968, 84

Contact with moisture under acidic conditions generates silanes which ignite in air.

See other METAL NON-METALLIDES

4693. Magnesium nitride

[12057-71-5] **Mg_3N_2**

$Mg^{2+}\ Mg^{2+}\ Mg^{2+}\quad N^{3-}\quad N^{3-}$

See entry REFRACTORY POWDERS

See other NITRIDES

4694. Magnesium phosphide

[12057-74-8] **Mg_3P_2**

$Mg^{2+}\ Mg^{2+}\ Mg^{2+}\quad P^{3-}\quad P^{3-}$

Oxidants

Mellor, 1940, Vol. 8, 842

It ignites on heating in chlorine, or in bromine or iodine vapours at higher temperatures. Reaction with nitric acid causes incandescence.

Water

Mellor, 1940, Vol. 8, 842

Phosphine is evolved and may ignite.

See other METAL NON-METALLIDES

4695. Manganese

[7439-96-5] **Mn**

Mn

NSC 306, 1982

Aluminium

Occup. Hazards, 1966, **28**(11), 44

The finely divided metal is pyrophoric, and a mixture of manganese and aluminium dusts accidentally released from a filter bag exploded violently.

Carbon dioxide

See Carbon dioxide: Metals

Other reactants

Yoshida, 1980, 352

MRH values calculated for 16 combinations with oxidants are given.

Oxidants MRH Chlorine 3.85/56, hydrogen peroxide 5.36/48, nitric acid 4.85/41

Mellor, 1942, Vol. 12. 186—188

Powdered manganese ignites and becomes incandescent in fluorine or on warming in chlorine. Contact with conc. hydrogen peroxide causes violent decomposition and/or ignition, and with nitric acid incandescence and a feeble explosion were observed.

See Ammonium nitrate: Metals MRH 3.80/69
Bromine pentafluoride: Acids, etc. MRH 4.52/65
Nitryl fluoride: Metals

Phosphorus

See Phosphorus: Metals

Sulfur dioxide

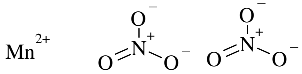
Mellor, 1942, Vol. 12, 187

Pyrophoric manganese burns brilliantly on warming in sulfur dioxide.

See other METALS, PYROPHORIC METALS

4696. Manganese(II) nitrate

[10377-66-9] **MnN_2O_6**



Other reactants

Yoshida, 1980, 206

MRH values calculated for 16 combinations with oxidisable materials are given.

Urea

Novikov, A. V. *et al., Chem. Abs.*, 1975, **82**, 48151

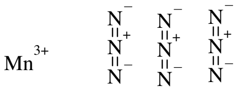
The anhydrous complex with urea finally decomposes at 240°C with a light explosion.

See also AMMINEMETAL OXOSALTS

See other METAL NITRATES

4697. Manganese(III) azide

[ ] (not isolated) **MnN_9**



Alkenes

1. Fristad, W. F. *et al., J. Org. Chem.*, 1985, **50**, 3647—3649
2. *Chem. Abs.,* **109**, 82979g

The preparation and immediate use of manganese(III) azide species generated slowly in situ by refluxing manganese(III) acetate and sodium azide in acetic acid in presence of alkene reaction substrates to prepare 1,2-diazidoalkanes avoids the need to isolate manganese(III) azide which has a high probability of explosive instability [1]. The (II) azide is known [20260-90-6], isolable, detonable and has been patented as a power source for lasers [2].

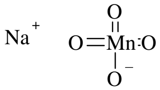
Styrene

See Sodium azide: Manganese(III) salts, Styrene

See related METAL AZIDES

4698. Sodium permanganate

[10101-50-5] **$MnNaO_4$**



Habits and thought patterns have been formed by the long established use of the potassium salt, which is about ten times less soluble. Much more immediately available energy can therefore be contrived when solutions of the sodium salt are mixed with reducants. This seems to be behind a rash of accidents.

Acetic acid, or Acetic anhydride

See Potassium permanganate: Acetic acid

Cellulose

See Sodium thiosulfate, below

Methanol

U.S. Office of Nuclear and Facility safety, Operating Experience Weekly Summary, 96-40, 1996

Sodium permanganate was used in place of the potassium salt in an experiment to degrade chlorinated materials in oils. Addition of methanol caused a violent reaction, spraying the mix about. The concentration, or acidity, of the material is not stated. However sodium permanganate is far more soluble in water, and presumably methanol, than is the potassium salt. Intimate mixing means more violent reaction.

Other reactants

Yoshida, 1980, 93

MRH values calculated for 20 combinations with oxidisable materials are given.

See other METAL OXOMETALLATES, OXIDANTS

Sodium thiosulfate

1. www.external.ameslab.gov/esha/lessons learned/Red_alerts/000929a, 2000
2. U.S. Office of Oversight, Type B Accident Report 00-11, 2000

Attempting to destroy several litres of residual 40% sodium permanganate solution, a tecnician added solid sodium thiosulfate to it. The 'bump' produced by superheating from reaction with this threw hot permanganate solution onto his jeans, which were also consumed where sprayed, in a reaction described as 'ignition'. He received severe burns.

4699. Manganese(II) oxide

[1344-43-0] **MnO**

$Mn{=}O$

Hydrogen peroxide

See Hydrogen peroxide: Metals, etc.

See other METAL OXIDES

4700. Manganese(IV) oxide (Manganese dioxide)

[1313-13-9] **MnO_2**

$O{=}Mn{=}O$

HCS 1980, 609

Aluminium

Sidgwick, 1950, 1265

Interaction on heating is very violent (a thermite reaction).

See Aluminium: Metal oxides

See other THERMITE REACTIONS

Anilinium perchlorate

See Anilinium perchlorate: Metal oxides

Calcium hydride

Pascal, 1958, Vol. 4, 304

Interaction becomes incandescent on warming.

See other REDOX REACTIONS

Carbon black, Chlorinated paraffin, Lead(IV) oxide, Manganese(IV) oxide

See Lead(IV) oxide: Carbon black, etc.

Diboron tetrafluoride

See Diboron tetrafluoride: Metal oxides

Hydrogen sulfide

See Hydrogen sulfide: Metal oxides

Hydroxylaminium chloride

See Hydroxylaminium chloride: Manganese dioxide

Lithium

Hamportzumian, K. *et al., J. Power Sources*, 1982, **8**, 35—40

Manganese dioxide—lithium batteries are generally safer than sulfur dioxide—lithium cells.

See Lithium: Sulfur dioxide

Oxidants MRH Chlorine trifluoride 1.80/52, hydrogen peroxide 1.59/99+

1. Mellor, 1942, Vol. 12, 254
2. Mellor, 1941, Vol. 1, 936
3. Ahrle, H., *Z. Angew. Chem.*, 1909, **22**, 713
4. von Schwartz, 1918, 323
5. Blanco Prieto, J., *Chem. Abs.*, 1976, **84**, 46791

Action of chlorine trifluoride causes incandescence [1]. Manganese dioxide catalytically decomposes powerful oxidising agents, often violently. Dropped into conc. hydrogen peroxide, the powdered oxide may cause explosion [2]. Either the massive or the powdered oxide explosively decomposes 92% peroxomonosulfuric acid [3], and mixtures with chlorates (‘oxygen mixture’, heated to generate the gas) may react with explosive violence [4]. Cuban pyrolusite can be used in place of potassium dichromate to promote thermal decomposition of potassium chlorate in match-head formulations [5].

See Peroxyformic acid: Metals, etc.

Potassium azide

Mellor, 1940, Vol. 8, 347

On gentle warming, interaction is violent.

See other METAL OXIDES, OXIDANTS

Rubidium acetylide

See Rubidium acetylide: Metal oxides

4701. Manganese(II) sulfide

[18820-29-6] MnS

$$Mn{=}S$$

Mellor, 1942, Vol. 12, 394

The vacuum-dried red sulfide becomes red-hot on exposure to air.

See other METAL SULFIDES, PYROPHORIC MATERIALS

4702. Manganese(IV) sulfide

[12125-23-4] MnS_2

$$MnS_2$$

Sorbe, 1968, 84

It explodes at 580°C.

See other METAL SULFIDES

4703. Manganese(II) telluride

[12032-88-1] **MnTe**

$Mn^{2+} \qquad Te^{2-}$

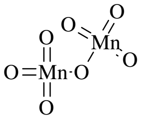
Lithium

See Lithium: Metal oxides, etc.

See other METAL NON-METALLIDES

4704. Manganese(VII) oxide

[12057-92-0] **Mn_2O_7**



1. Mellor, 1942, Vol. 12, 293
2. Bailar, 1973, Vol. 3, 805

An unstable powerful oxidant, it explodes between 40 and 70°C, or on friction or impact, sensitivity being as great as that of mercury fulminate [1]. Detonation occurs at 95°C, and under vacuum explosive decomposition occurs above 10°C [2].

See Potassium permanganate: Sulfuric acid

Organic material

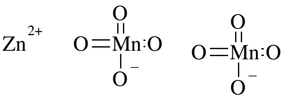
1. Patterson, A. M., *Chem. Eng. News*, 1948, **26**, 711
2. Mellor, 1940, Vol. 12, 293

A sample of the heptoxide exploded in contact with the grease on a stopcock [1], and explosion or ignition has been noted with various solvents, oils, fats and fibres [2].

See other METAL OXIDES, OXIDANTS

4705. Zinc permanganate

[23414-72-4] **Mn_2O_8Zn**



$$Zn^{2+} \quad O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^{-}}{|}}{Mn}}{=}O \quad O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^{-}}{|}}{Mn}}{=}O$$

Cellulose

Sörgel, U. C., *Pharm. Prax., Beil. Pharmaz.*, 1960, (2), 30

An explosion involved contact of the permanganate with cellulose.

Organic compounds

Wolfe, S. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 7755—7757

Solid zinc permanganate and magnesium permanganate react violently with many classes of organic compounds. The reactions may be controlled successfully by supporting the oxidants on silica. The zinc salt is more effective than the magnesium salt, but both are much more reactive than potassium permanganate.
See other METAL OXOMETALLATES, OXIDANTS

4706. Manganese phosphide
[12263-33-1] **Mn_3P_2**

$Mn^{2+}\ Mn^{2+}\ Mn^{2+}\ P^{3-}\ P^{3-}$

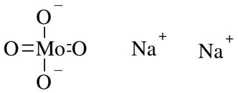
Chlorine
See Chlorine: Phosphorus compounds
See other METAL NON-METALLIDES

4707. Molybdenum
[7439-98-7] **Mo**

Mo

Oxidants — MRH value shows % of oxidant
See Bromine pentafluoride: Acids, etc.
Bromine trifluoride: Halogens, etc.
Chlorine trifluoride: Metals
Fluorine: Metals — MRH 7.57/54
Iodine pentafluoride: Metals
Lead(IV) oxide: Metals
Nitryl fluoride: Metals
Potassium perchlorate: Metal powders
Sodium peroxide: Metals
See other METALS

4708. Sodium molybdate
[10102-40-6] **$MoNa_2O_4$**



$O{=}Mo(O^-)_2{=}O\quad Na^+\quad Na^+$

Aniline, Nitrobenzene
Nolan, 1983, Case history 144
In the preparation of a dyestuff from aniline, nitrobenzene (as oxidant), hydrochloric acid and sodium hydroxide, ferric chloride is often used as catalyst, but sodium molybdate was substituted as a more effective catalyst. The materials were charged

into a 4.5 m^3 reactor and heating was started after addition of nitrobenzene, but the temperature controller was mis-set, and overheating at a high rate ensued. The exotherm was much higher than normal because of the more effective catalyst, and partial failure of the cooling water led to an uncontrollable exotherm.
See other METAL OXOMETALLATES, RUNAWAY REACTIONS

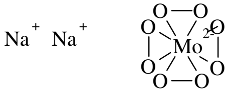
4709. Molybdenum nitride

[37245-81-1] [12033-19-1] MoN; [12033-31-7] Mo_2N; [97953-19-0] Mo_4N Mo_nN
Complex structures

Nitric acid
Chorley, R. W., *Chem. Brit.*, 1993, **29**(10), 867
High surface area samples may be pyrophoric, but can be passivated by exposure to oxygen. A passivated sample (50 mg) caused a small explosion when concentrated nitric acid was added to it.
See also MIXING
See other NITRIDES

4710. Sodium tetraperoxomolybdate

[42489-15-6] (ion) $MoNa_2O_8$



Castrantas, 1965, 5
It decomposes explosively under vacuum.
See other PEROXOACID SALTS

4711. Molybdenum(IV) oxide

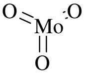
[18868-43-4] MoO_2

$$O{=}Mo{=}O$$

Gibson, 1969, 102
It becomes incandescent in contact with air.
See other METAL OXIDES, PYROPHORIC MATERIALS

4712. Molybdenum(VI) oxide

[1313-27-5] MoO_3



Graphite
1. Young, J. A., private comm., 1989; *CHAS Notes*, 1992, **X**(6), 2
2. Partington, 1967, 753

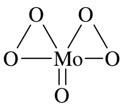
During preparation of an alloy steel, molybdenum trioxide (372 kg), and then graphite (340 kg, 1.56 equiv., in 4 portions), were charged into an electric furnace containing a charge of melted scrap steel at 1500—1600°C, using a charging ram and rotatable box for the additions through the furnace door. Immediately after the last graphite addition, as the ram and box were being withdrawn, a large fireball emerged through the furnace door and fatally burned the ram operator. This was caused by the very rapid exothermic redox reaction between the oxide and graphite to give molybdenum and a huge volume (some 800 m^3) of very hot carbon monoxide) which emerged at high velocity from the 27 m^3 furnace and ignited, giving a flame-jet some 15 m long and 2—3 m in diameter [1]. It is possible that some of the graphite particles were ejected in the gas jet and augmented the combustion intensity. Reduction of the trioxide to molybdenum by strongly heating with carbon has long been a commercial metallurgical process [2].
See other REDOX REACTIONS

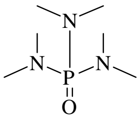
Interhalogens
See Bromine pentafluoride: Acids, etc.
Chlorine trifluoride: Metals. etc.

Metals
Mellor, 1943, Vol. 11, 542
Reduction of the oxide by heated sodium or potassium proceeds with incandescence, and explosion occurs in contact with molten magnesium.
See Lithium: Metal oxides
See other METAL OXIDES

4713. Oxodiperoxomolybdenum—hexamethylphosphoramide

[53474-95-6 + 680-31-9] **$MoO_5.C_6H_{18}N_3OP$**





Fieser, 1974, Vol. 4, 203
The monohydrated complex exploded after storage at ambient temperature for a month. Refrigerated storage is recommended.
See related AMMINECHROMIUM PEROXOCOMPLEXES, METAL PEROXIDES

4714. Molybdenum(IV) sulfide

[1317-33-5] **MoS_2**

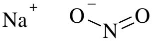
MoS_2

Magnesium
Danielyan, N. G. *et al., Mod. Phys. Lett. B.*, 1991, **5**(19), 1301

Molybdenum disulphide is capable of forming a thermite type mixture with magnesium, which may explode on grinding.
See also THERMITE REACTIONS

Potassium nitrate
See Potassium nitrate: Metal sulfides
See other METAL SULFIDES

4715. Sodium nitrite
[7632-00-0] **$NNaO_2$**



FPA H133, 1984; *HCS 1980*, 852

Aminoguanidine salts
Urbanski, 1967, Vol. 3, 207
Interaction, without addition of acid, produces tetrazolylguanidine (‘tetrazene’), a primary explosive of equal sensitivity to mercury(II) azide, but more readily initiated.

Ammonium salts MRH Ammonium chloride 1.80/44, nitrate 1.46/99+
1. von Schwartz, 1918, 299
2. Mellor, 1967, Vol. 8, Suppl. 2.1, 388
3. *RoSPA Occ. Safety and Health Suppl.*, 1972, **2**(10), 32

Heating a mixture of an ammonium salt with a nitrite salt causes a violent explosion on melting [1], owing to formation and decomposition of ammonium nitrite. Salts of other nitrogenous bases behave similarly. Mixtures of ammonium chloride and sodium nitrite are used as commercial explosives [2]. Accidental contact of traces of ammonium nitrate with sodium nitrite residues caused wooden decking on a truck to ignite [3].
See Wood, below
See also NITRITE SALTS OF NITROGENOUS BASES

1,3-Butadiene
1. Beer, R. N., private comm., 1972
2. Keister, R. G. *et al., Loss. Prev.*, 1971, **5**, 69

Sodium nitrite solution is used to inhibit ‘popcorn’ polymerisation of butadiene in processing plants. If conc. nitrite solutions (5%) are used, a black sludge is produced, which when dry, will ignite and burn when heated to 150°C, even in absence of air [1]. The sludge produced from use of nitrite solutions to scavenge oxygen in butadiene distillation systems contained 80% of organic polymer and a nitrate:nitrite ratio of 2:1. Use of dilute nitrite solution (0.5%) or pH above 8 prevents sludge formation [2].
See Buten-3-yne: 1,3-Butadiene
See Nitrogen oxide: Dienes

Hydroxylamine hydrochloride
Scott, E. S., *J. Chem. Ed.*, 1992, **69**(12), 1028

If hydroxylamine hydrochloride and sodium nitrite, of normal laboratory particle size, are swiftly shaken together and left to stand, a vigorous gas evolving reaction will start after a short induction period. This is a rare example of spontaneous reaction of solids [though both materials are hygroscopic and presumably have a surface water film in which the Editor imagines reaction to start].
See Ammonium salts, above

Maize husks, Sodium nitrate
See Sodium nitrate: Maize husks, etc.

Metal amidosulfates
Heubel, J. *et al., Compt. rend.*, 1963, **257**, 684—686
Interaction of nitrites when heated with metal amidosulfates (sulfamates) may become explosively violent owing to liberation of nitrogen and steam. Mixtures with ammonium sulfamate form ammonium nitrite which decomposes violently around 80°C.
See Sodium nitrate: Metal amidosulfates

Metal cyanides

1. von Schwartz, 1918, 299
2. Mellor, 1940, Vol. 8, 478
3. Greenwood, P. H. S., *J. Proc. R. Inst. Chem.*, 1947, 137
4. Elson, C. H. R., *J. Proc. R. Inst. Chem.*, 1947, 19
5. Eiter, K. *et al.*, Austrian Pat. 176 784, 1953

Mixtures of sodium nitrite and various cyanides [1] explode on heating, including potassium cyanide [2], potassium hexacyanoferrate(III), sodium pentacyanonitrosylferrate(II) [3], potassium hexacyanoferrate(II) [4], or mercury(II) cyanide [5]. Such mixtures have been proposed as explosives, initiable by heat or a detonator [5].

Other reactants
Yoshida, 1980, 13
MRH values calculated for 19 combinations with oxidisable materials are given.

Paper, Sulfur
Anon., *CIHSC Chem. Safety Summ.*, 1984, **55**(218), 36
Empty paper sacks, some of which had contained sulfur or inorganic salts but mostly sodium nitrite, were dumped (with general rubbish) into a skip located inside by windows in direct sunlight. The fire which resulted was probably caused by exothermic interaction of the sodium nitrite with sulfur and damp paper, with further self heating aided by the generally insulating nature of the mound of paper sacks in the draught-free skip warmed by sunlight.
See Wood, below
See other SELF-HEATING AND GNITION INCIDENTS

Phenol
Hatton, J. P., private comm., 1976
A mixture exploded violently on heating in a test tube.

Phthalic acid, or Phthalic anhydride

Hawes, B. V. W., *J. R. Inst. Chem.*, 1955, **79**, 668

Mixtures of sodium nitrite and phthalic acid or phthalic anhydride explode violently on heating. A nitrite ester may have been produced.

See ACYL NITRITES

Potassium thiocyanate MRH (sodium salt) 3.57/28

1. Mellor, 1940, Vol. 8, 478
2. Baum, R., *Chem. Eng. News*, 1982, **60**(41), 29
3. Fawcett, H. H., *Chem. Eng. News*, 1982, **60**(46), 4
4. Shriver, D. F., also Coleman, L. F., *Chem. Eng. News*, 1982, **60**(47), 2
5. Pinsky, B., *Chem. Eng. News*, 1982, **60**(47), 2
6. Viola, A., *Chem. Eng. News*, 1983, **61**(3), 76

A mixture of the nitrite with sodium thiocyanate explodes on heating [1]. Preparation of a molten salt bath from 0.45 kg of potassium thiocyanate (reducant) and 1.35 kg of sodium nitrite (oxidant) led to a violent explosion on melting, which caused severe structural damage to the laboratory [2]. It was claimed that this could not have been foreseen from available information [2], but this was vigorously refuted [3,4]. Use of sand baths, rather than salt baths for laboratory heating purposes is to be preferred [5]. The relative lack of descriptive chemistry in modern curricula is cited as the major contributory factor to the general ignorance which led to the explosion [6].

See METAL THIOCYANATES: Oxidants, MOLTEN SALT BATHS

See other REDOX REACTIONS

Reducants

See Potassium thiocyanate, above

See Sodium disulfite, below

See Sodium nitroxylate

See Sodium thiosulfate, below

Sodium amide

Bergstrom, F. W. *et al., Chem. Rev.*, 1933, **12**, 64

Addition of solid sodium nitrite to the molten amide caused immediate gas evolution, followed by a violent explosion.

Sodium disulfite MRH 1.84/68

MCA Case History No. 183

Large-scale addition of solid sodium disulfite to an unstirred and too-concentrated solution of sodium nitrite caused a vigorous exothermic reaction.

See other REDOX REACTIONS

Sodium nitrate, Sodium sulfide

Janz, 1976, Table 3, 22

Accidental mixing of the 3 molten salts caused a violent explosion.

See other REDOX REACTIONS

Sodium thiocyanate

See Potassium thiocyanate, above

See other REDOX REACTIONS

Sodium thiosulfate

Mellor, 1940, Vol. 8, 478; 1947, Vol. 10, 501

There is no interaction between solutions, but evaporation of the mixture gave a residue which explodes on heating. The mixed solids behave similarly.

See other REDOX REACTIONS

Urea MRH 2.80/30

Bucci, F., *Ann. Chim.* (Rome), 1951, **41**, 587

Fusion of urea (2 mol) with sodium nitrite (or potassium nitrite, 1 mol of either) to give high yields of the cyanate must be carried out exactly as described to avoid the risk of explosion.

Wood

Anon., *ABCM Quart. Safety Summ.*, 1944, **15**, 30

Wooden staging, which had become impregnated over a number of years with sodium nitrite, became accidentally ignited and burned as fiercely as if impregnated with potassium chlorate. Although the effect of impregnating cellulosic material with sodium nitrate is well known, that due to sodium nitrite was unexpected.

See Ammonium salts (reference 3)

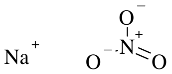
See also Paper above

See also Sulfur, above

See other METAL NITRITES, METAL OXONON-METALLATES, OXIDANTS

4716. Sodium nitrate

[7631-99-4] **$NNaO_3$**



FPA H26, 1983; *HCS 1980*, 851

Acetic anhydride

See Acetic anhydride: Metal nitrates

Aluminium MRH Aluminium 4.43/27

1. Anon., *Fire*, 1935, **28**, 30
2. Farnell, P. L. *et al., Chem. Abs.*, 1972, **76**, 129564
3. Gerling, H. W., *Metall* (Berlin), 1982, **36**, 698—699

Mixtures of the nitrate with powdered aluminium or its oxide (the latter seems unlikely) were reported to be explosive [1], and the performance characteristics of flares containing compressed mixtures of the metal and nitrate have been evaluated [2]. A violent explosion in a copper smelting works was caused mainly by reaction of aluminium with sodium nitrate [3].

Aluminium, Water

Jackson, B. *et al., Chem. Abs.*, 1976, **84**, 46798

During investigation of pyrotechnic flare formulations, it was found that mixtures of the metal powder and oxidant underwent a low-temperature exothermic reaction at 70—135°C in presence of moisture.

Antimony

Mellor, 1939, Vol. 9, 382

Powdered antimony explodes when heated with an alkali metal nitrate.

Arsenic trioxide, Iron(II) sulfate

Dunn., B. W., *Bur. Expl. Rept. 13*, Pennsylvania, Amer. Rail Assoc., 1920

A veterinary preparation containing the oxidant and reducant materials (possibly with some additional combustibles) ignited spontaneously.

See other REDOX REACTIONS

Barium thiocyanate

Pieters, 1957, 30

Mixtures may explode

See Sodium thiocyanate, below

Bitumen

1. Xu, Y.-C. *et al., Chem. Abs.*, 1980, **93**, 209761
2. Yu, M.-H. *et al., J. Haz. Mat.*, 2004, **113**(1-3), 165

The induction periods for the reaction of sodium nitrate—bitumen mixtures (43:57 wt) heated at 195, 234 or 260°C are 44, 2 and 0.5 h, respectively. Further study of sodium nitrate/bitumenised waste systems held at these temperatures showed an initial weak exotherm around 260°C and a larger exotherm (0.96—1.21 kJ/g) accompanied by 50% wt loss around 430°C [1]. Following an actual accident while encapsulating nuclear waste the system has been re-examined. With small nitrate crystal size, the mixing process can potentially give runaway from little above 160°C, by initial surface reaction slowly warming until the salt melts, whereupon exothermicity sharply increases [2].

See other NUCLEAR WASTES

Boron phosphide

Mellor, 1940, Vol. 8, 845

Deflagration occurs in contact with molten alkali metal nitrates.

Calcium—silicon alloy

Smolin, A. O., *Chem. Abs.*, 1974, **81**, 138219

Combustion of the alloy in admixture with sodium nitrate is mentioned in an explosives context, but no details are translated.

Fibrous material — MRH Cellulose 3.85/30

1. Mellor, 1961, Vol. 2, Suppl. 2.1, 1244
2. Anon., *ABCM Quart. Safety Summ.*, 1944, **15**, 30

Fibrous organic material (jute storage bags) is oxidised in contact with sodium nitrate above 160°C and will ignite below 220°C [1]. Wood and similar cellulosic materials are rendered highly combustible by nitrate impregnation [2].

Jute, Magnesium chloride

van Hoogstraten, C. W., *Chem. Abs.*, 1947, **41**, 3692b

Solid crude sodium nitrate packed in jute bags sometimes ignited the latter in storage. Normally ignition did not occur below 240°C, but in cases where magnesium chloride (up to 16%) was present, ignition occurred at 130°C. This was attributed to formation of magnesium nitrate hexahydrate, which hydrolyses above its m.p. (90°C) liberating nitric acid. The latter was thought to have caused ignition of the jute bags under unusual conditions of temperature and friction.

See Magnesium nitrate: Dimethylformamide

Magnesium MRH 8.58/42

Bond, B. D. *et al., Combust. Flame*, 1966, **10**, 349—354

A study of the kinetics in attack of magnesium by molten sodium nitrate indicates that decomposition of the nitrate releases oxygen atoms which oxidise the metal so exothermally that ignition ensues.

See Magnesium: Metal oxosalts

Maize husks, Sodium nitrite

Anon., *CISHC Chem. Safety Summ.*, 1985, **52**(222), 66

A rotary drum had been used previously to dry metal components which had been heat-treated in nitrate—nitrite molten salt baths, washed, then tumble dried with ground maize husks to absorb adhering water. When the drum was taken out of service, it was not cleaned out. After some 10 months it was recommissioned, but while being heated up to operating temperature, an explosion occurred which ejected flame jets for several m. This was attributed to presence of considerable contamination of the maize husks by metal nitrate—nitrite residues, and ignition on heating of such material was confirmed experimentally.

See MOLTEN SALT BATHS

Metal amidosulfates

Heubel, J. *et al., Compt. rend.*, 1962, **255**, 708—709

Interaction of nitrates when heated with amidosulfates (sulfamates) may become explosively violent owing to liberation of dinitrogen oxide and steam.

See Sodium nitrite: Metal amidosulfates

Metal cyanides MRH Sodium cyanide 4.31/37

See MOLTEN SALT BATHS

Non-metals MRH Phosphorus (r) 4.43/27, sulfur 3.39/24

1. Mellor, 1941, Vol. 2, 820
2. Leleu, *Cahiers*, 1980, (99), 279

Contact of powdered charcoal with the molten nitrate, or of the solid nitrate with glowing charcoal, causes vigorous combustion of the carbon. Mixtures with charcoal and sulfur have been used as black powder [1]. Charcoal powder—nitrate mixtures burn briskly at 200°C [2].

Other reactants

Yoshida, 1980, 199

MRH values calculated for 19 combinations with oxidisable materials are given.

Peroxyformic acid

See Peroxyformic acid: Sodium nitrate

Phenol, Trifluoroacetic acid

Spitzer, U. A. *et al., J. Org. Chem.*, 1974, **39**, 3936

When the salt—acid nitration mixture was applied to phenol, a potentially hazardous rapid exothermic reaction occurred producing tar.

See other NITRATION INCIDENTS

Sodium MRH 3.85/57

Mellor, 1961, Vol. 2, Suppl. 2.1, 518

Interaction of sodium nitrate and sodium alone, or dissolved in liquid ammonia, eventually gives a yellow explosive compound.

See Sodium nitroxylate

Sodium nitrite, Sodium sulfide

See Sodium nitrite: Sodium nitrate, Sodium sulfide

Sodium phosphinate MRH 1.00/56

Mellor, 1941, Vol. 2, 820

A mixture exploded violently on warming.

See other REDOX REACTIONS

Sodium thiocyanate

Anon., *Sichere Chemiearbeit*, 1994, **46**, 80

Sodium nitrate and sodium thiocyanate were being blended in a ploughshare mixer to produce a plating formulation. The blend deflagrated, burning four workers and blowing apart the mixer. Subsequent laboratory investigation showed such mixtures to be friction sensitive. The firm has ceased to prepare such mixtures. Caution is advised when mixing oxidants and reducants.

Sodium thiosulfate

Mellor, 1941, Vol. 2, 820

A mixture is explosive when heated.

See other REDOX REACTIONS

Tris(cyclopentadienyl)cerium

1. Jakob, K., *Z. Anorg. Allg. Chem.*, 1988, **556**, 170
2. Grodett, P. S., *Chem. Eng. News*, 1988, **66**(31), 2

Reaction of ammonium hexanitrocerate and cyclopentadienylsodium under inert conditions gives tris(cyclopentadienyl)cerium and sodium nitrate, removed by filtration before evaporation of solvent [1]. When the filtration step was omitted, and the evaporated solid mixture was heated to 75°C, a violent explosion occurred. This may have involved complexes of the type $Ce(NO_3)Cp_2 \cdot NaNO_3$ [2], but a direct redox reaction between the reactive $CeCp_3$ and the oxidant is also possible.

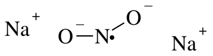
See other REDOX REACTIONS

Wood

See Fibrous material, above

See other METAL NITRATES, OXIDANTS

4717. Sodium nitroxylate
[13968-14-4] **NNa_2O_2**



Air, or Carbon dioxide, or Water

Mellor, 1963, Vol. 2, Suppl. 2.2, 1566

The solid is very reactive towards air, moisture or carbon dioxide, and tends to explode readily, also decomposing violently on heating. It is produced from sodium nitrate or sodium nitrite by electrolytic reduction, or action of sodium.

See other N—O COMPOUNDS

4718. Sodium nitride
[12136-83-3] **NNa_3**

$Na^+ \quad Na^+ \quad Na^+ \quad N^{3-}$

Fischer, F. *et al., Ber.*, 1910, **43**, 1468

It decomposes explosively on gentle warming.

See other NITRIDES

4719. Nitrogen oxide ('Nitric oxide')
[10102-43-9] **NO**

N=O

1. *UK Sci. Mission Rept. 68/79*, Washington, UKSM, 1968
2. Miller, R. O., *Ind. Eng. Chem., Proc. Res. Dev.*, 1968, **7** 590—593
3. Ribovich, J. *et al., J. Haz. Mat.*, 1977, **1**, 275—287
4. Ramsay, J. B. *et al., Proc. 6th Int. Symp. Detonation*, 1976, 723—728
5. U.S. Chemical Safety and Hazard Investigation Board, *Case Study 2003-15-C-OH*, 2004

Liquid nitrogen oxide and other cryogenic oxidisers (ozone, fluorine in presence of water) are very sensitive to detonation in absence of fuel, and can be initiated as readily as glyceryl nitrate [1,2]. Detonation of the endothermic liquid oxide close to its b.p. (—152°C) generated a 100 kbar pulse and fragmented the test equipment. It is the simplest molecule that is capable of detonation in all 3 phases [3]. The liquid oxide is sensitive and may explode during distillation [4]. This has been the cause of industrial accident [5].

It is highly endothermic (ΔH_f° (g) +90.4 kJ/mol, 3.01 kJ/g) and an active oxidant.

Acetone, base

Arulsamy, N. *et al., J. Amer. Chem Soc.*, 2001, **123**(44), 10860

Reaction of acetone with nitric oxide in presence of alkali alkoxides gives various diazene *N*-oxide- *N*'-hydroxylate salts (RN(O)=NOMet, also called diazenediolates), such as the disodium methanebis- or trisodium methanetris- compounds according to nitric oxide pressure. Potassium alkoxides behaved similarly, but lithium only formed a bis- compound. These compounds are explosive. The sodium bis- hydrate shattered a DSC apparatus.

See also Acetonitrile, base, next below

Acetonitrile, base

See Sodium methanetris(diazeniumdiolate)

Acetylene, Perchloric acid

See Perchloric acid: Acetylene, Nitric oxide

Alkenes, Oxygen

See Nitrogen dioxide: Alkenes

Ammonia

Checkel, M. D. *et al., J. Loss Prevention*, 1995, **8**(4), 215

Flammability limits of mixtures of nitric oxide and ammonia were studied. The limits are 15 —70% ammonia; tenfold pressure rise and explosion are possible. Introduction of oxygen into flammable compositions will produce autoignition, via nitrogen dioxide formation, contamination with air might.

Carbon disulfide

Winderlich, R., *J. Chem. Educ.*, 1950, **27**, 669

A demonstration of combustion of carbon disulfide in nitrogen oxide (both endothermic compounds) exploded violently.

Carbon, Potassium hydrogen tartrate

Pascal, P. *et al., Mém. Poudres*, 1953, **35**, 335—347

The ignition temperature of 400°C for carbon black in nitrogen oxide was reduced by the presence of the tartrate.

Dichlorine oxide

See Dichlorine oxide: Nitrogen oxide

Dienes, Oxygen

1. Haseba, S. *et al., Chem. Eng. Progr.*, 1966, **62**(4), 92
2. Schuftan, P. M., *Chem. Eng. Progr.*, 1966, **62**(7), 8

Violent explosions which occurred at —100 to —180°C in ammonia synthesis gas units were traced to the formation of explosive addition products of dienes and oxides of nitrogen, produced from interaction of nitrogen oxide and oxygen. Laboratory experiments showed that the addition products from 1,3-butadiene or cyclopentadiene formed rapidly at about —150°C, and ignited or exploded on warming to —35 to —15°C. The unconjugated propadiene, and alkenes or acetylene reacted slowly and the products did not ignite until +30 to +50°C [1]. This type of derivative

('pseudo-nitrosite') was formerly used (Wallach) to characterise terpene hydrocarbons. Further comments were made later [2].
See Sodium nitrite: 1,3-Butadiene

Fluorine
See Fluorine: Non-metal oxides

Hydrogen, Nitrous oxide
Glowinski, J. *et al., Przem. Chem.*, 1996, **75**(2), 63
Explosive limits for this combination have been studied from 1 to 20 bar at 50°C.

Hydrogen, Oxygen
Chanmugam, J. *et al., Nature*, 1952, **170**, 1067
Pre-addition of nitrogen oxide (or nitrosyl chloride as its precursor) to stoicheiometric hydrogen—oxygen mixtures at 240 mbar/360°C will cause immediate ignition under a variety of circumstances.

Metal acetylides or carbides
Mellor, 1946, Vol. 5, 848, 891
Rubidium acetylide ignites on heating, and uranium dicarbide incandesces in the gas at 370°C.

Metals
Mellor, 1940, Vol. 8, 436; 1943, Vol. 11, 162; 1942, Vol. 12, 32
Pyrophoric chromium attains incandescence in the oxide, while calcium, potassium and uranium need heating before ignition occurs, when combustion is brilliant in the 53% oxygen content.

Methanol
Partel, G., *Riv. Ing.*, 1965, **15**, 969—976
This oxidant—fuel system was evaluated as a rocket propellant combination.

Nitrogen trichloride
See Nitrogen trichloride: Initiators

Non-metals
Mellor, 1940, Vol. 8, 109, 433, 435
Amorphous (not crystalline) boron reacts with brilliant flashes at ambient temperature, and charcoal or phosphorus continue to burn more brilliantly than in air (which has a much lower oxygen content).

Nucleophiles
Reaction of nucleophiles with nitric oxide, in presence of bases, if the nucleophile itself be not one, can form diazenediolates, often reacting more than once. Products anywhere near oxygen balance are likely to prove explosive.

Ozone
See Ozone: Nitrogen oxide

Pentacarbonyliron
Manchot, W. *et al., Ann.*, 1929, **470**, 275

Rapid heating to above 50°C in an autoclave caused an explosive reaction.

Perchloryl fluoride
See Perchloryl fluoride: Hydrocarbons, etc.

Phosphine, Oxygen
Mellor, 1940, Vol. 8, 435
Addition of oxygen to a mixture of phosphine and nitrogen oxide causes explosion.
See Phosphine: Oxygen

Potassium sulfide
Mellor, 1940, Vol. 8, 434
The pyrophoric sulfide ignites in the oxide.

Sodium diphenylketyl

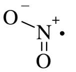
1. Mendenhall, D., *J. Amer. Chem. Soc.*, 1974, **96**, 5000
2. Mendenhall, D., *Chem. Eng. News*, 1982, **60**(20), 2

A procedure for preparation of sodium hyponitrite involving reduction of nitrogen oxide by the ketyl, followed by extraction into water [1], had been operated routinely on the small scale. A 41-fold scaled up run exploded and ignited after 200 ml of water had been added as part of the work-up. This was attributed to the presence of an unusually large proportion of coagulated unreacted sodium in the ketyl. Small-scale operation with precautions is urged [2].

Vinyl chloride
See Vinyl chloride: Oxides of nitrogen
See other ENDOTHERMIC COMPOUNDS, NON-METAL OXIDES, OXIDANTS

4720. Nitrogen dioxide (Dinitrogen tetraoxide)

[10102-44-0] **NO_2**



At ambient temperatures the title gases exist as an equilibrium mixture; for details *See* Dinitrogen tetraoxide

Alkenes
Rozlovskii, A. I., *Chem. Abs.*, 1975, **83**, 118122
The mechanisms of explosions in solidified gas mixtures at low temperatures containing unsaturated hydrocarbons and oxides of nitrogen is discussed. Fast radical addition of nitrogen dioxide to double bonds is involved, and with dienes it is a fast reaction of very low energy of activation. Possibilities of preventing explosions are discussed.
See Nitrogen oxide: Dienes, Oxygen
See other NON-METAL OXIDES, OXIDANTS

4721. Plutonium nitride
[12033-54-4] **NPu**

$$Pu^{3+} \quad N^{3-}$$

Oxygen, Water

Bailar, 1973, Vol. 5, 343

The ignition temperature of the nitride in oxygen is lowered from 300° to below 100°C by the presence of moisture.

See other NITRIDES

4722. Rubidium nitride
[12136-85-5] **NRb_3**

$$Rb^{+} \quad Rb^{+} \quad Rb^{+} \quad N^{3-}$$

Mellor, 1940, Vol. 8, 99

The alkali nitrides burn in air.

See other N-METAL DERIVATIVES

4723. Poly(sulfur nitride)
[56422-03-8] **$(NS)_n$**

Complex Structure

Kennet, F. A. *et al., J. Chem. Soc., Dalton Trans.*, 1982, 851—857

Hazards involved in various routes to the polymer are detailed.

See Caesium azide: Sulfur dioxide

See also Poly(selenium nitride)

See other NITRIDES, N—S COMPOUNDS

4724. Antimony(III) nitride
[12333-57-2] **NSb**

$$Sb^{3+} \quad N^{3-}$$

Alone, or Water

1. Fischer, F. *et al., Ber.*, 1910, **43**, 1471
2. Franklin, E. C., *J. Amer. Chem. Soc.*, 1905, **27**, 850

Explosive decomposition occurs on warming under vacuum [1] and impure material explodes mildly on heating in air, or on contact with water or dilute acids.

See other NITRIDES

4725. Poly(selenium nitride)
[12033-59-9] **$(NSe)_n$**

Complex Structure

Preparative hazard

See Trimethylsilyl azide: Selenium halides

See also Poly(sulfur nitride)

See other NITRIDES

See related N—S COMPOUNDS

4726. Thallium(I) nitride

[12033-67-9] **NTl**

$Tl^{3+} \quad N^{3-}$

Alone, or Water

Mellor, 1940, Vol. 8, 262

The nitride explodes violently on exposure to shock, heat, water or dilute acids.

See other NITRIDES

4727. Uranium(III) nitride

[25658-43-9] **NU**

$U^{3+} \quad N^{3-}$

Bailar, 1973, Vol. 5, 340

Finely powdered material is pyrophoric on exposure to air at ambient temperature.

See other NITRIDES, PYROPHORIC MATERIALS

4728. Zirconium nitride

[25658-42-8] **NZr**

$Zr^{3+} \quad N^{3-}$

See entry REFRACTORY POWDERS

See other NITRIDES

4729. Nitrogen (Gas)

[7727-37-9] **N_2**

$N{\equiv}N$

Kletz, T. A., *Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 1519—1527, Basle, SSCI, 1980

The benefits of large scale use of nitrogen as an inerting gas to prevent fire or explosion have been at the expense of many fatal asphyxiations arising from its accidental use in place of air or from its unexpected presence in confined spaces. At an oxygen concentration below 10%, collapse is almost instantaneous. Various accidents are described with appropriate precautions, and it was concluded that nitrogen may have killed more people than any other single substance in industry.

Lithium
See Lithium (reference 1)
See also Lithium: Metal chlorides

Lithium tetrahydroaluminate
See Lithium tetrahydroaluminate: Nitrogen

Ozone
See Ozone: Nitrogen

Titanium
See Titanium: Nitrogen

4730. Nitrogen (Liquid)

[ ] **N_2**

$N{\equiv}N$

1. Anon., *BCISC Quart. Safety Summ.*, 1964, **35**, 25
2. Anon., *BCISC Quart.Safety Summ.*,1974, **45**, 11
3. Lindsay, W. N., *Chem. Eng. News*, 1987, **65**(24), 2

Although liquid nitrogen is inherently safer than liquid oxygen or liquid air as a coolant, its ability to condense liquid oxygen out of the atmosphere can create hazards. A distillation tube containing a little solvent was cooled in liquid nitrogen while being sealed off in a blowpipe flame. A few minutes late the tube exploded, probably owing to high internal pressure caused by evaporation of liquid oxygen which had condensed into the tube during sealing. It is possible the atmosphere close to the blowpipe was oxygen-enriched. Open vessels which contain organic materials, or which are to be hermetically sealed should not be cooled in liquid nitrogen but in a coolant at a higher temperature. Liquid nitrogen should normally be used only for cooling evacuated or closed vessels where extreme cooling is necessary, and it should be removed from around the vacuum trap or other vessel before opening them to atmosphere [1]. The later reference describes 2 incidents of forceful explosion of 75 l cryogenic containers of liquid nitrogen. The cause of the first appeared to be blockage of the 19 mm neck by an ice-plug formed in a very humid environment. The cause of the second was probably ‘roll-over’ of a surface layer of superheated liquid, and fracture of the vessel by the ensuing violent boil-off of gas. Superheating of 10—15°C is known to occur in high-purity liquid nitrogen, but much higher levels of superheating may be possible. Various remedies (stirring, generation of a warm spot or vertical submerged conductive gauzes) are discussed [2]. With the current heightened interest in new materials which become superconducting at liquid nitrogen temperature (—195.8°C), the attention of workers (not necessarily chemists) in this area is drawn to the fact that containers of liquid nitrogen exposed to atmosphere inevitably will condense some oxygen (b.p. —183°C) into the nitrogen coolant. Such mixtures may behave as an oxidant and react violently with traces of oil, grease or other organic material. Vacuum flasks of liquid nitrogen should not be left about unused or uncovered [3].

Argon

See Argon: Liquid nitrogen

Fatty materials

Anon., *CISHC Chem Safety Summ.*, 1979, **50**, 91

Use of liquid nitrogen in cryogenic grinding of fatty materials led to an explosion. Condensation of liquid oxygen onto the fatty material, with initiation by the grinding friction seems a likely causative sequence.

Hydrogen

See Hydrogen (Gas): Liquid nitrogen

Magnesium

Ephraim, 1939, 625

A mixture of magnesium powder and liquid nitrogen reacts very violently when lit with a fuse, forming magnesium nitride.

Oxygen, Radiation

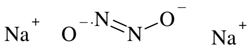
1. Chen, C. W. *et al., Cryogenics*, 1969, **9**, 131—132
2. Takehisa, M. *et al., Chem. Abs.*, 1977, **87**, 30593
3. Perdue, P. T., *Health Phys.*, 1972, **23**, 116—117
4. Watanabe, H. *et al., Chem. Abs.*, 1980, **92**, 30294

Liquid nitrogen subject to nuclear radiation (high neutron and gamma fluxes) must be kept free of oxygen to prevent explosions occurring in reactor cryostats. The explosive species generated is not nitrogen oxide or nitrogen dioxide, because solutions of these will not cause explosion on contact with a drop of acrylonitrile, whereas irradiated oxygen-containing nitrogen does so. Ozone was thought to be responsible [1], and this was confirmed by a detailed experimental investigation [2], though trace organic impurities may also have been involved [1]. The subject has been reviewed, and oxygen must also be eliminated from liquid helium, hydrogen or noble gases before irradiation [3]. Similar effects and conclusions were associated with an explosion which occurred when liquid nitrogen was used to cool a target during electron-beam irradiation [4].

See other CRYOGENIC LIQUIDS, IRRADIATION DECOMPOSITION INCIDENTS

4731. Sodium hyponitrite

[100435-20-9] **$N_2Na_2O_2$**



Preparative hazard

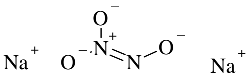
See Hyponitrous acid

See Nitrogen oxide: Sodium diphenylketyl

See also Sodium amide (reference 4)

4732. Sodium trioxodinitrate

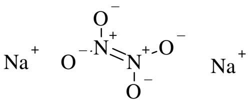
[13826-64-7] **$N_2Na_2O_3$**



See Sodium amide (reference 4)
See other METAL NITRATES

4733. Sodium tetraoxodinitrate

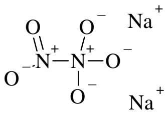
[ ] **$N_2Na_2O_4$**



See Sodium amide (reference 4)
See other METAL NITRATES

4734. Sodium pentaoxodinitrate

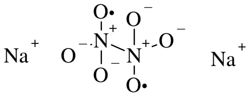
[59795-18-5] **$N_2Na_2O_5$**



See Sodium amide (reference 4)
See other METAL NITRATES

4735. Sodium hexaoxodinitrate

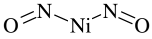
[ ] **$N_2Na_2O_6$**



See Sodium amide (reference 4)
See other METAL NITRATES

4736. Dinitrosylnickel

[ ] **N_2NiO_2**



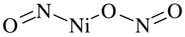
Mond, R. L. *et al., J. Chem. Soc.*, 1922, **121**, 38

A blue, impure and probably polymeric solid, produced from reaction of nitric oxide and nickel carbonyl, decomposed with incandescence at 90°C. The structure is very doubtful but a dinitrosyl was tentatively postulated. A trinitrosyl, [115380-62-6], has been listed more recently.

See other HEAVY METAL DERIVATIVES, NITROSO COMPOUNDS

4737. Nitritonitrosylnickel

[ ] **N_2NiO_3**



Water

Bailar, 1973, Vol. 3, 1119

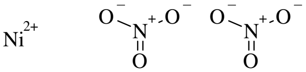
It is probably polymeric and ignites on contact with water.

See other NITROSO COMPOUNDS

See related METAL NITRITES

4738. Nickel(II) nitrate

[13138-45-9] **N_2NiO_6**



Oxidant. The tetrammine and tetrahydrazine complexes are explosive.

See AMMINEMETAL NITRATES, METAL NITRATES: Organic matter

1-Methylbenzotriazole

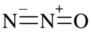
Diamantopoulou, E. *et al., Polyhedron*, 1994, **13**(10), 1593

A study of the 1-methylbenzotriazole complexes, of various stoicheiometry and hydration, showed several to be explosive.

See other METAL NITRATES, OXIDANTS

4739. Dinitrogen oxide (‘Nitrous oxide’)

[10024-97-2] **N_2O**



FPA H111, 1982 (cylinder); *HCS 1980*, 692 (cylinder)

1. Rüst, 1948, 278
2. Conrad, D. *et al., Chem. Abs.*, 1983, **99**, 55875
3. Editorial feature, *Reading Times* (PA), 14th May, 1987
4. Bretherick, L., *Chem. Eng. News*, 1987, **65**(31), 3
5. Hamsen, B. *et al., Chem. Eng. News*, 1991, **69**(29), 2

During transfer of the liquefied gas from a stock steel cylinder into smaller cylinders, the effective expansion caused cooling of the stock cylinder and a fall in pressure to occur. Application of a flame to the stock cylinder of the endothermic oxide led to decomposition and explosive rupture of the cylinder [1]. The explosive decomposition of the gas at 0.05—8 bar at ambient temperature after initiation by electric discharge can be prevented by addition of 30 vol% of air, nitrogen or oxygen [2]. Oxyacetylene welding repair work on or near to a 6 t tank of liquefied oxide led to a violent explosion [3], effectively a large scale rerun 85 years after the original incident described above [4]. When using nitrous oxide, containing organic solutes, as a supercritical fluid for hplc purposes, a 1 ml sample exploded, causing considerable shrapnel damage. It is recommended that it be not used as a supercritical fluid [5].

It is highly endothermic (ΔH_f° (g) +90.4 kJ/mol, 2.01 kJ/g) and an active oxidant.
See Fuels, below
See also INDIGESTION
See other ENDOTHERMIC COMPOUNDS

Acetylene
See ATOMIC ABSORPTION SPECTROSCOPY

Boron
Mellor, 1940, Vol. 8, 109
Amorphous boron (not crystalline) ignites on heating in the dry oxide.

Carbon monoxide
Wilton, C. *et al., Chem. Abs.*, 1975, **82**, 113724
Possible blast hazards associated with use of the propellant combination liquid dinitrogen oxide—liquid carbon monoxide have been evaluated.

Combustible gases
Sorbe, 1968, 131
The oxide (with an oxygen content 1.7 times that of air) forms explosive mixtures with ammonia, carbon monoxide, hydrogen, hydrogen sulfide and phosphine.

Fuels
1. L. Bretherick's comments
2. Young, J. A., *CHASNotes*, 1993, **XI**(6), 2

Although the oxygen in dinitrogen oxide is chemically (but endothermically) bound to nitrogen, it is present in a much higher concentration (36.4%) than the 21% present in air in admixture with nitrogen, so combustion or oxidation in the oxide will be much faster than in air. Advantage of this has been taken by feeding the oxide together with air into carburettor intakes to boost internal combustion engine performance, but strict control is necessary to prevent premature ignition. Nitrogen oxide, though of even higher oxygen content (53.3%), is too reactive and corrosive for this application [1].

A man habitually enjoyed the euphoric effects of inhaling whiffs of nitrous oxide in seclusion, and kept a cylinder of the gas in his sedan for that purpose. He decided to spray the faded car seats with an aerosol can of vinyl dressing (propane/butane propellant) with the windows closed. Then he had a whiff of gas from the briefly

opened cylinder, and settled back to enjoy the euphoria and a cigarette. He was lucky to survive the resulting explosion of the fuel/oxidant mixture in a closed vessel [2].
See OXYGEN ENRICHMENT

Hydrazine
Mellor, 1967, Vol. 8, Suppl. 2.2, 214
Ignition occurs on contact.
See other REDOX REACTIONS

Hydrogen, Nitric oxide
See Nitrogen oxide: Hydrogen, etc.

Hydrogen, Oxygen
Bailar, 1973, Vol. 2, 321—322
The ignition temperature of mixtures of hydrogen with dinitrogen oxide is lower than that of hydrogen admixed with air or oxygen. The oxide also sensitises mixtures of hydrogen and oxygen, so that addition of oxygen to a hydrogen—oxide mixture will cause instaneous ignition or explosion. Explosive limits are extremely wide.

Lithium hydride
Mellor, 1967, Vol. 8, Suppl. 2.2, 214
The hydride ignites in the gas.

Phosphine
Thénard, J., *Compt. rend.*, 1844, **18**, 652
A mixture with excess oxide can be exploded by sparking.

Plastic tubes
See Oxygen (Gas): Plastic tubes

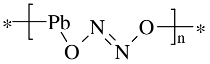
Preparative hazard
Bailar,1973, Vol. 2, 317

Silane
See Silane: Nitrogen oxides

Tin(II) oxide
See Tin(II) oxide: Non-metal oxides

Tungsten carbides
See Tungsten carbide: Nitrogen oxides
Ditungsten carbide: Oxidants
See other NON-METAL OXIDES, OXIDANTS

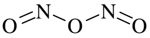
4740. Lead hyponitrite
[19423-89-3] **N_2O_2Pb**



Partington, J. R. *et al., J. Chem. Soc.*, 1932, 135, 2589

The lead salt decomposes with explosive violence at 150—160°C and should not be dried by heating. The salt prepared from lead acetate explodes more violently than that from the nitrate.
See other HEAVY METAL DERIVATIVES, N—O COMPOUNDS

4741. Dinitrogen trioxide
[10544-73-7] **N_2O_3**



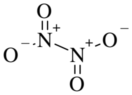
Acetic acid, 6-Hexanelactam
See 6-Hexanelactam: Acetic acid, etc.

Chloroprene
See 2-Chloro-1-nitro-4-nitroso-2-butene

Phosphine
See Phosphine (reference 3)

Phosphorus
See Phosphorus: Non-metal oxides
See other NON-METAL OXIDES, OXIDANTS

4742. Dinitrogen tetraoxide (Nitrogen dioxide)
[10544-72-6] **N_2O_4**



HCS 1980, 675 (cylinder)

The equilibrium mixture of nitrogen dioxide and dinitrogen tetraoxide is completely associated at —9°C to the latter form which is marginally endothermic (ΔH_f° (g) +9.7 kJ/mol, 0.10 kJ/g). Above 140°C it is completely dissociated to nitrogen dioxide, which is moderately endothermic (ΔH_f° (g) +33.8 kJ/mol, 0.74 kJ/g).

Acetonitrile, Indium MRH Acetonitrile 7.87/25
Addison, C. C. *et al., Chem. & Ind.*, 1958, 1004
Shaking a slow-reacting mixture caused detonation, attributed to indium-catalysed oxidation of acetonitrile.

Alcohols
Daniels, F., *Chem. Eng. News*, 1955, **33**, 2372
A violent explosion occurred during the ready interaction to produce alkyl nitrates.

Ammonia MRH 6.61/33
Mellor, 1940, Vol. 8, 541
Liquid ammonia reacts explosively with the solid tetraoxide at —80°C, while aqueous ammonia reacts vigorously with the gas at ambient temperature.

Barium oxide
Mellor, 1940, Vol. 8, 545
In contact with the gas at 200°C the oxide suddenly reacts, reaches red heat and melts.

Boron trichloride
Mellor, 1946, Vol. 5, 132
Interaction is energetic.

Carbon disulfide
1. Mellor, 1940, Vol. 8, 543
2. Sorbe, 1968, 132

Liquid mixtures proposed for use as explosives are stable up to 200°C [1], but can be detonated by mercury fulminate, and the vapours by sparking [2].

Carbonylmetals
Cloyd, 1965, 74
Combination is hypergolic.

Cellulose, Magnesium perchlorate
See Magnesium perchlorate: Cellulose, etc.

Cycloalkenes, Oxygen
Lachowicz, D. R. *et al.*, US Pat. 3 621 050, 1971
Contact of cycloalkenes with a mixture of dinitrogen tetraoxide and excess oxygen at temperatures of 0°C or below produces nitroperoxonitrates of the general formula —$CHNO_2$—$CH(OONO_2)$— which appear to be unstable at temperatures above 0°C, owing to the presence of the peroxonitrate group.
See Hydrocarbons, below

Difluorotrifluoromethylphosphine
Mahler, W., *Inorg. Chem.*, 1979, **18**, 352
A reaction, to produce the phosphine oxide on 12 mmol scale, ignited.

Dimethyl sulfoxide MRH 6.99/36
See Dimethyl sulfoxide: Dinitrogen tetraoxide

Formaldehyde
1. Pollard, F. H. *et al., Trans. Faraday Soc.*, 1949, **45**, 767—770
2. Rastogi, R. P. *et al., Chem. Abs.*, 1975, **83**, 12936

The slow (redox) reaction becomes explosive around 180°C [1], or even lower [2].
See other REDOX REACTIONS

Halocarbons
MRH Chloroform 2.38/67, 1,2-dichloroethane 5.06/42, 1,1-dichloroethylene 5.06/46, trichloroethylene 3.97/56
1. Turley, R. E., *Chem. Eng. News*, 1964, **42**(47), 53
2. Benson, S. W., *Chem. Eng. News*, 1964, **42**(51), 4
3. Shanley, E. S., *Chem. Eng. News*, 1964, **42**(52), 5
4. Kuchta, J. M. *et al., J. Chem. Eng. Data*, 1968, **13**, 421—428

Mixtures of the tetraoxide with dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, trichloroethylene and tetrachloroethylene are explosive when subjected to shock of 25 g TNT equivalent or less [1]. Mixtures with trichloroethylene react violently on heating to 150°C [2]. Partially fluorinated chloroalkanes were more stable to shock. Theoretical aspects are discussed in the later reference [2,3]. The effect of pressure on flammability limits has been studied [4].

See Uranium: Nitric acid

See Vinyl chloride: Oxides of nitrogen

Heterocyclic bases MRH Pyridine 7.82/22, quinoline 7.87/22

Mellor, 1940, Vol. 8, 543

Pyridine and quinoline are attacked violently by the liquid oxide.

Hydrazine derivatives

1. Cloyd, 1965, 74
2. Miyajima, H. *et al., Combust. Sci. Technol.*, 1973, **8**, 199—200

Combinations with hydrazine, methylhydrazine, 1,1-dimethylhydrazine or mixtures thereof are hypergolic and used in rocketry [1]. The hypergolic gas-phase ignition of hydrazine at 70—160°C/53—120 mbar has been studied [2].

See ROCKET PROPELLANTS

Hydrocarbons MRH values below references

1. Mellor, 1967, Vol. 8, Suppl. 2.2, 264
2. Fierz, H. E., *J. Soc. Chem. Ind.*, 1922, **41**, 114R
3. Raschig, F., *Z. Angew. Chem.*, 1922, **35**, 117—119
4. Berl, E. *Z. Angew. Chem.*, 1923, **36**, 87—91
5. Schaarschmidt, A., *Z. Angew. Chem.*, 1923, **36**, 533—536
6. Berl, E., *Z. Angew. Chem.*, 1924, **37**, 164—165
7. Schaarschmidt, A., *Z. Angew. Chem.*, 1925, **38**, 537—541
8. *MCA Case History No. 128*
9. Folecki, J. *et al., Chem. & Ind.*, 1967, 1424
10. Cloyd, 1965, 74
11. Urbanski, 1967, Vol. 3, 289
12. Biasutti, 1981, 50
13. Biasutti, 1981, 53—54

MRH Benzene 7.99/19, hexane 7.91/17, isoprene 8.28/18, methylcyclohexane 7.87/17

A mixture of the tetraoxide and toluene exploded, possibly initiated by unsaturated impurities [1]. During attempted separation by low temperature distillation of an accidental mixture of light petroleum and the oxide, a large bulk of material awaiting distillation became heated by unusual climatic conditions to 50°C and exploded violently [2]. Subsequently, discussion of possible alternative causes involving either unsaturated or aromatic compounds was published [3,4,5,6,7]. Erroneous addition of liquid in place of gaseous nitrogen tetraoxide to hot cyclohexane caused an explosion [8]. During kinetic studies, one sample of a 1:1 molar solution of tetraoxide in hexane exploded during (normally slow) decomposition at 28°C [9]. Cyclopentadiene is hypergolic with the oxide [10]. These incidents are understandable because of their similarity to rocket propellant systems and liquid mixtures previously used as bomb

fillings [11]. The liquid oxide leaking from a ruptured 6 t storage tank ran into a gutter containing toluene and a violent explosion ensued [12]. An alternative account describes the hydrocarbon as benzene [13].
See Cycloalkenes, above; Unsaturated hydrocarbons, below

Hydrogen, Oxygen
Lewis, B., *Chem. Rev.*, 1932, **10**, 60
The presence of small amounts of the oxide in non-explosive mixtures of hydrogen and oxygen renders them explosive.

Isopropyl nitrite, Propyl nitrite
Safety in the Chemical Laboratory, Vol. 1, 121, Steere, N. V. (Ed.), Easton (Pa.) *J. Ch. Ed.*, 1967
A pressurised mixture of the cold components exploded very violently during a combustion test run. The mixture was known to be autoexplosive at ambient temperature, and both of the organic components are capable of violent decomposition in absence of added oxidant.

Laboratory grease
Arapava, L. D. *et al., Chem. Abs.*, 1985, **102**, 169310
Contact of the lubricating grease Litol-24 with the oxidant at below 80°C led to explosion on subsequent impact. This involved nitration products of the antioxidant present, 4-hydroxydiphenylamine. Above 80°C decomposition superceded nitration, and no explosion occurred.
See other NITRATION INCIDENTS

Metal acetylides or carbides MRH values show % of oxidant
Mellor, 1946, Vol. 5, 849
Caesium acetylide ignites at 100°C in the gas.
See Tungsten carbide: Nitrogen oxides MRH 4.02/63
Ditungsten carbide: Oxidants MRH 3.85/67

Metals MRH Magnesium 12.97/50, potassium 3.72/46
1. Mellor, 1940, Vol. 8, 544—545; 1942, Vol. 13, 342
2. Pascal, 1956, Vol. 10, 382; 1958, Vol. 4, 291

Reduced iron, potassium and pyrophoric manganese all ignite in the gas at ambient temperature. Magnesium filings burn vigorously when heated in the gas [1]. Slightly warm sodium ignites in contact with the gas, and interaction with calcium is explosive [2].
See Aluminium: Oxidants

Nitroaniline
Anon., *CISHC Chem. Safety Summ.*, 1978, **49**, 3—4
Process errors led to discharge of copious amounts of nitrous fumes into the glass reinforced plastic ventilation duct above a diazotisation vessel. On two occasions fires were caused in the duct by vigorous reaction of the dinitrogen tetraoxide with nitroaniline dusts in the duct. Laboratory tests confirmed this to be the cause of the fires, and precautions are detailed.

Nitroaromatics

1. Urbanski, 1967, Vol. 3, 288
2. Kristoff, F. T. *et al., J. Haz. Mat.*, 1983, **7**, 199—210

Mixtures with nitrobenzene were formerly used as liquid high explosives, with addition of carbon disulfide to lower the freezing point, but high sensitivity to mechanical stimulus was disadvantageous [1]. During the recovery of acids from nitration of toluene, mixtures of the oxide with nitrotoluene or dinitrotoluene may be isolated under certain process conditions. While such mixtures are not unduly sensitive to impact, friction or thermal initiation, when oxygen-balanced they are extremely sensitive to induced shock and are capable of explosive propagation at film thicknesses below 0.5 mm. It is suspected that many explosions in TNT acid recovery operations, previously attributed to tetranitromethane, may have been caused by such mixtures [2].

Nitrogen trichloride

See Nitrogen trichloride: Initiators

Organic compounds

Riebsomer, J. L., *Chem. Rev.*, 1945, **36**, 158

In a review of the interaction of the oxidant with organic compounds, attention is drawn to the possibility of formation of unstable or explosive products.

Other reactants

Yoshida, 1980, 269

MRH values calculated for 18 combinations with oxidisable materials are given.

Ozone

See Ozone: Nitrogen oxide

Phospham

See Phospham: Oxidants

Phosphorus MRH 9.12/35

See Phosphorus: Non-metal oxides

Sodium amide

Beck, G., *Z. Anorg. Chem.*, 1937, **233**, 158

Interaction with the oxide in carbon tetrachloride is vigorous, producing sparks.

Steel, Water

U.S. National Transportation Safety Board, Hazardous Materials Accident Brief, Jan. 1998

A carbon steel tank for rail transportation of the tetroxide became contaminated with water, probably when a leaking valve, later replaced, was hosed down. After repair, the tank was charged with 50 tons of the oxide. This was later found to be wet, attempts were than made to empty the tanker. Acording to the single meter used to measure the transfer, this was accomplished (subsequent investigation suggested that only about 3 tons had been transferred because the dip pipes had corroded away). Water was charged to wash out the tank. The sequence of supposed emptying and washing was repeated and more water was added. It was noticed that pressure and fumes were excessive, atempts to deal with this continued some days. About a month after initial loading, and ten days after first washing, one of the heads blew off, throwing cladding about 100 m. Inspection of the remains showed several bands of corrosion, caused by nitric acid, produced from the oxide and water, reacting with steel to produce hydrogen and/or lower oxides of nitrogen which pressurised the weakened tank. Large tank cars are no longer used.

Tetracarbonylnickel
Bailar, 1973, Vol. 3, 1130
Interaction of the liquids is rather violent.
See Carbonylmetals, above

Tetramethyltin
Bailar, 1973, Vol. 2, 355
Interaction is explosively violent even at —80°C, and dilution with with inert solvents is required for moderation.

2-Toluidinium nitrate
Rastogi, R. P. *et al., Indian J. Chem., Sect. A*, 1980, **19**A, 317—321
Reaction in this hybrid rocket propellant system is enhanced by presence of ammonium vanadate.

Triethylamine
Davenport, D. A. *et al., J. Amer. Chem. Soc.*, 1953, **75**, 4175
The complex, containing excess oxide over amine, exploded at below 0°C when free of solvent.

Triethylammonium nitrate
Addison, C. C. *et al., Chem. & Ind.*, 1953, 1315
The two component form an addition complex with diethyl ether, which exploded violently after partial desiccation: an ether-free complex is also unstable.
See Triethylamine, above

Unsaturated hydrocarbons MRH Isoprene 8.28/18
1. Sergeev, G. P. *et al., Chem. Abs.*, 1966, **65**, 3659g
2. Biasutti, 1981, 123

Dinitrogen tetraoxide reacts explosively between —32° and —90°C with propene, 1-butene, isobutene, 1,3-butadiene, cyclopentadiene and 1-hexene, but 6 other unsaturates failed to react [1]. Reaction of propene with the oxide at 2 bar/30°C to give lactic acid nitrate was proceeding in a pump-fed tubular reactor pilot plant. A violent explosion after several hours of steady operation was later ascribed to an overheated pump gland which recently had been tightened. A similar pump with a tight gland created a hot-spot at 200°C [2].
See Nitrogen dioxide: Alkenes

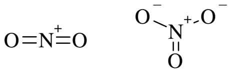
Vinyl chloride
See Vinyl chloride: Oxides of nitrogen

Xenon tetrafluoride oxide
Christe, K. O., *Inorg. Chem.*, 1988, **27**, 3764

In the reaction of the pentaoxide with xenon tetrafluoride oxide to give xenon difluoride dioxide and nitryl fluoride, the xenon tetrafluoride oxide must be used in excess to avoid formation of xenon trioxide, which forms a sensitive explosive mixture with xenon difluoride dioxide.
See Xenon tetrafluoride oxide: Caesium nitrate
See other ENDOTHERMIC COMPOUNDS, NON-METAL OXIDES, OXIDANTS

4743. Dinitrogen pentaoxide (Nitryl nitrate)

[10102-03-1] **N_2O_5**



Partington, 1967, 569
If suddenly heated, the solid (m.p. 30°C) explodes. The structure is now considered to be nitryl nitrate.

Acetaldehyde
Kacmarek, A. J. *et al., J. Org. Chem.*, 1975, **40**, 1853
Direct combination to produce ethylidene dinitrate at —196°C is violently explosive, but uneventful when the acetaldehyde is diluted with nitrogen.

Aromatic compounds
Editor's comments, 1999
Increased availability of this oxide means it is finding use as a clean and mild nitrating agent. A stoichiometric byproduct in many procedures is anhydrous nitric acid, which is often blithely ignored. Anhydrous nitric acid is a very hazardous material in its own right, being surprisingly unreactive – except as an oxidant during detonations! In particular, work-up by distillation is virtually certain to form detonable compositions in the condenser at some stage. The editor is not yet aware of any accidents during such distillation, but counsels forethought.
See Nitric acid

tert-Butylhydroperoxide, Toluene
See tert-Butylhydroperoxide: Toluene, Dinitrogen pentaoxide

Dichloromethane
See NITRATING AGENTS

Ethylene
Nitro Compounds, Feuer H. & Nielsen A. T. (Eds), New York, VCH, 1990, 315
The crude product is too explosive to be worked up. Analogy with other olefins indicates that the final product will be ethylene glycol dinitrate, a known explosive though safe enough to have largely replaced nitroglycerine. That will be preceded by 1,2-dinitroethane and nitratonitroethane, more sensitive if less powerful.

Metals
Mellor, 1940, Vol. 8, 554

Potassium and sodium burn brilliantly in the gas, while mercury and arsenic are vigorously oxidised.

Naphthalene

Mellor, 1940, Vol. 8, 554

Naphthalene explodes and other organic materials react vigorously with the powerful oxidant.

Sodium acetylide

See Sodium acetylide: Oxidants

Strained ring heterocycles

Golding, P. *et al., Tetrahedron Lett.*, 1988, **29**, 2731—2734; 2735—2736

Strained ring oxygen heterocycles such as epoxides and oxetanes react with the oxide in dichloromethane at sub-ambient temperatures to form high yields of the powerfully explosive glycol dinitrate esters. Epoxides give 1,2-dinitrates (such as those from ethylene, propene, butene and 4 other oxides), while oxetanes (6 examples) give 1,3-dinitrates. Strained ring nitrogen heterocycles give explosive *N*-nitroaminoalkyl nitrates, and several derived from aziridines and 3 derived from azetidines are exemplified.

See NITRATING AGENTS

See other STRAINED-RING COMPOUNDS

Sulfur dichloride, or Sulfuryl chloride

Schmeisser, M., *Angew. Chem.*, 1955, **67**, 495, 499

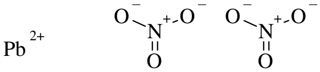
Interaction is explosively violent.

See other NON-METAL OXIDES, OXIDANTS

See related ACID ANHYDRIDES

4744. Lead(II) nitrate

[10099-74-8] **N_2O_6Pb**



HCS 1980, 589

Calcium—silicon alloy

Smolin, A. O., *Chem. Abs.*, 1975, **85**, 7591

'Combustion of Calcium—Silicon in a Mixture with Lead Nitrate' (title only translated)

Carbon MRH 1.76/7

Mellor, 1941, Vol. 7, 863

Contact with red hot carbon causes an explosion with showers of sparks.

Cyclopentadienylsodium

Houben-Weyl, 1975, Vol. 13.3, 200

If lead nitrate is used rather than the chloride or acetate as the source of divalent lead, the crude dicyclopentadienyllead may explode violently during purification by high-vacuum sublimation at 100—130°C.

Other reactants

Yoshida, 1980, 200

MRH values for 17 combinations with oxidisable materials are given.

Potassium acetate

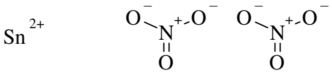
Mee, A. J., *School Sci. Rev.*, 1940, **28**(86), 95

A heated mixture of the oxidant and organic salt exploded violently.

See other METAL NITRATES, OXIDANTS

4745. Tin(II) nitrate

[22755-27-7] **N_2O_6Sn**



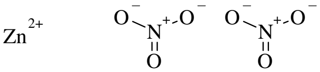
Bailar, 1973, Vol. 2, 74

During attempted isolation of the nitrate by evaporation of its aqueous solutions, a number of explosions have occurred.

See other METAL NITRATES, REDOX COMPOUNDS

4746. Zinc nitrate

[7779-88-6] **N_2O_6Zn**



HCS 1980, 967

Carbon

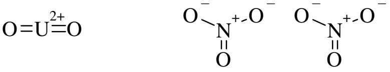
Mellor, 1940, Vol. 4, 655

When the nitrate is sprinkled on to hot carbon, an explosion occurs.

See other METAL NITRATES, OXIDANTS

4747. Uranyl nitrate

[10102-06-4] **N_2O_8U**



Cellulose

Clinton, T. G., *J. R. Inst. Chem.*, 1958, **82**, 633

The analytical use of cellulose fibre to absorb uranyl nitrate solution prior to ignition has led to explosions during ignition, owing to formation of cellulose nitrate. An alternative method is descibed.

Diethyl ether

1. Ivanov, W. N., *Chem. Ztg.*, 1912, **36**, 297
2. Andrews, L. W., *J. Amer. Chem. Soc.*, 1912, **34**, 1686—1687
3. Müller, A., *Chem. Ztg.*, 1916, **40**, 38; 1917, **41**, 439

The mild detonations reported when the crystalline salt was disturbed [1] were thought to have been caused by presence of solvent ether in the crystals (6 mols of water may be replaced by 2 of ether) [2]. This was later confirmed [3], and the formation of ethyl nitrate or diethyloxonium nitrate may have been involved, as the anhydrous salt functions as a powerful nitrator. Solutions of the nitrate in ether should not be exposed to sunlight to avoid the possibility of explosions.

See Organic solvents, below

See other IRRADIATION DECOMPOSITION INCIDENTS

Ethylene glycol

See Ethylene glycol: Oxidants

Organic solvents

Burriss, W. H., *Nucl. Sci. Abs.*, 1976, **33**, 19790

During routine operations to reduce the hexahydrate to uranium trioxide, an excessive amount of organic solution entered the denitrator pots and ignited.

See Diethyl ether, above

See also NITRATING AGENTS

See other METAL NITRATES

4748. Lead nitride

[58572-21-7] **N_2Pb_3**

$$Pb^{2+} \quad Pb^{2+} \quad Pb^{2+} \quad N^{3-} \quad N^{3-}$$

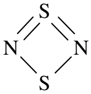
Fischer, F. *et al., Ber.*, 1910, **43**, 1470

Very unstable, it decomposes explosively during vacuum degassing.

See other NITRIDES

4749. Disulfur dinitride

[25474-92-4] **N_2S_2**



1. Brauer, 1963, Vol. 12, 410
2. Williams, J. D., *Polyhedron*, 1987, **6**(5), 939—941

Explosive, initiated by shock, friction, pressure or temperatures over 30°C [1]. It may also detonate spontaneously at ambient temperature [2].

Metal chlorides

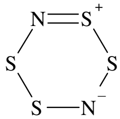
Roesky, H. W. *et al., Inorg. Chem.*, 1984, **23**, 75

The 1:1 complexes with beryllium chloride or titanium tetrachloride may explode violently.

See other NITRIDES, N—S COMPOUNDS

4750. Tetrasulfur dinitride

[32607-15-1] **N_2S_4**



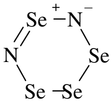
1. Brauer, 1963, Vol. 1, 408
2. Heal, H. G. *et al., J. Inorg. Nucl. Chem.*, 1975, **37**, 286

It decomposes explosively to its elements at 100°C. Previously prepared from the explosive tetranitride [1], it may now safely be prepared from the stable intermediate, heptasulfur imide [2].

See other NITRIDES, N—S COMPOUNDS

4751. Tetraselenium dinitride

[132724-39-1] **N_2Se_4**



Dehnicke, K. *et al., Angew. Chem. (Int.)*, 1991, **30**(5), 577

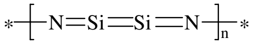
Made from diselenium dichloride and trimethylsilyl azide, the crystalline nitride explodes under a hammer blow, or on heating to 80°C. Can apparently be handled safely at room temperature.

See other NITRIDES

See related N—S COMPOUNDS

4752. Poly(disilicon nitride)

[12438-96-9] **$(N_2Si_2)_n$**



Alone, or Water

Gmelin, 1959, Vol. 15.B, 610

It ignites in air, explodes on heating and contact with drops of water generates sparks.

See other NITRIDES

4753. Sodium azide

[26628-22-8] **N_3Na**

$$Na^{+} \quad \overset{-}{N}{=}\overset{+}{N}{=}N^{-}$$

HCS 1980, 827

1. Mellor, 1940, Vol. 8, 345
2. Lambert, B., *School Sci. Rev.*, 1927, **8**(31), 218
3. Anon., *Jahresber.*, 1981, 77—79
4. Anon., *Safety*, 1982, (3), 2
5. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
6. www.chemsafety. gov/circ. US Chem. Safety & Haz. Investigation Board, CSB 2001-5086
7. Hagenbuch, J-P. *Chimia*, 2003, **57**(12), 773

Insensitive to impact, it decomposes, sometimes explosively, above its m.p. [1], particularly if heated rapidly [2]. Although used in aqueous solutions as a preservative in pharmaceutical preparations, application of freeze-drying techniques to such solutions has led to problems arising from volatilisation of traces of hydrazoic acid from non-neutral solutions, condensation in metal lines, traps or filters, and formation of heavy metal azides in contact with lead, copper or zinc components in the drying plant [3,4]. An explosion is reported when cutting into a pipe previously used to transport the powdered azide [air may have been involved as an oxidant – Ed.] [6]. A study of risks inherent in industrial use of sodium azide at hundred kg scale is reported. For reagent use, keeping the mix buffered to alkalinity is important [7]

Energy of exothermic decomposition in range 230—260°C was measured as 0.76 kJ/g by DSC, and T_{ait24} was determined as 253°C by adiabatic Dewar tests, with an apparent energy of activation of 145 kJ/mol [5].

See Heavy metals, below

Acids

See Hydrogen azide

Ammonium chloride, Trichloroacetonitrile

See 5-Trichloromethyltetrazole

Barium carbonate

Henneburg, G. O. *et al., Can. J. Res.*, 1950, **28B**, 345

Interaction to form cyanide ion requires careful control of temperature at 630°C to prevent explosions.

Bromine

See Bromine: Metal azides

Carbon disulfide

Stohlmeier, M. *et al., Chem. Ind. Dig.*, 1993, **6**(2), 124

A review on all the more or less explosive products which may be prepared from the above, with advice on safe handling and preparation.

See also Carbon disulfide: Metal azides

Carbonyl dichloride (Phosgene)
See tert-Butyl azidoformate (reference 4)

Chloroform
See Dichloromethane: Quaternary ammonium azides, etc.

Chromyl chloride
See Chromyl chloride: Sodium azide

Cyanuric chloride
See 2,4,6-Triazido-1,3,5-triazine (reference 2)

Dichloromethane, Dimethyl sulfoxide

1. Peet, N. P. *et al., Chem. Eng. News*, 1993, **71**(16), 4
2. Hruby, V. J. *et al., Chem. Eng. News*, 1993, **71**(41), 2

An explosion was experienced during work up of an epoxide opening reaction involving acidified sodium azide in a dichloromethane/dimethyl sulfoxide solvent. The author ascribes this to diazidomethane formation from dichloromethane [1]. A second report of an analoguous accident, also attributed to diazidomethane, almost certainly involved hydrogen azide for the cold traps of a vacuum pump on a rotary evaporator were involved; this implies an explosive more volatile than dichloromethane. It is recommended that halogenated solvents be not used for azide reactions [2].
See Dichloromethane: Quaternary ammonium azides, etc.

2,5-Dinitro-3-methylbenzoic acid, Oleum
See 2,5-Dinitro-3-methylbenzoic acid: Oleum, Sodium azide

Heavy metals

1. Wear, J. O., *J. Chem. Educ.*, 1975, **52**, A23—25
2. Becher, H. H., *Naturwiss.*, 1970, **57**, 671
3. Anon., *Chem. Eng. News*, 1976, **54**(36), 6
4. Pobiner, H., *Chem. Eng. News*, 1982, **60**(125), 4
5. Anon., *Safety Digest Univ. Safety Assoc.*, 1992, **44**, 22
6. Kurtz, L., Internet, 1995
7. Mellor, 1967, Vol. 8, Suppl. 2, 4

The effluent from automatic blood analysers in which 0.01—0.1% sodium azide solutions are used, may lead over several months to formation of explosive heavy metal azides in brass, copper or lead plumbing lines, especially if acids are also present. Several incidents during drain-maintenance are described, and preventative flushing and decontamination procedures are discused [1]. Brass plates, exposed to sodium azide solution during several months in soil-percolation tests and then dried, caused explosions owing to formation of copper and/or zinc azides [2]. During repairs to a metal thermostat bath in which sodium azide had been used as a preservative, a violent explosion occurred [3]. Use of sodium azide in automatic sulfur titrators led to explosions arising from formation of copper azide in a copper/brass valve assembly [4]. Mixing sodium azide solutions with heavy metal salts will produce the metal azides with greater facility; an explosion with mercuric chloride is reported [5]. A similar incident is reported later, apparently the mixture has been recommended as a biocide for aqueous solutions. In this case an explosion occurred while stirring water containing perhaps 5% of each [6]. Raney nickel catalyses the vigorous decomposition of solutions of hydrogen azide or azide salts [7].

Manganese(III) salts, Styrene

Fristad, W. E. *et al., J. Org. Chem.*, 1985, **50**, 3468

After applying an apparently safe procedure for diazidation of alkenes to styrene, an explosion occurred as the clear solution was cooling.

Nitryl fluoride

Klapötke, T. M. *et al., Chem. Ber.*, 1994, **127**(11), 2181

Reaction with sodium azide even at —78°C leads to explosions attributed to fluorine azide formation.

See Fluorine azide

Sulfuric acid

Ross, F. F., *Water & Waste Treatment*, 1964, **9**, 528; private comm., 1966

One of the reagents required for the determination of dissolved oxygen in polluted water is a solution of sodium azide in 50% sulfuric acid. It is important that the diluted acid should be quite cold before adding the azide, since hydrogen azide boils at 36°C and is explosive in the condensed liquid state.

Trifluoroacryloyl fluoride

See Trifluoroacryloyl fluoride: Sodium azide

Water

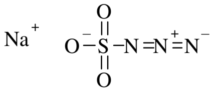
Anon., *Angew. Chem.*, 1952, **64**, 169

Addition of water to sodium azide which had been heated strongly caused a violent reaction. This was attributed to formation of metallic sodium or sodium nitride.

See other METAL AZIDES

4754. Sodium azidosulfate

[67880-15-3] **N_3NaO_3S**



$$Na^{+}\quad {}^{-}O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-N=\overset{+}{N}=N^{-}$$

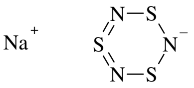
Shozda, R. J. *et al., J. Org. Chem.*, 1967, **32**, 2876

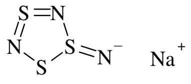
It is a weak explosive with variable sensitivity to mechanical shock and heating.

See other ACYL AZIDES

4755. Sodium trisulfurtrinitridate

[65107-36-0] (ion) **N_3NaS_3**





Bojes, J. *et al., Inorg. Chem.*, 1978, **17**, 319

Like tetrasulfur tetranitride, salts of trisulfur trinitride and of pentasulfur tetranitride (particularly alkali-metal salts) are heat- and friction-sensitive explosives. Preparation on a scale limited to 1 g, and care in use of spatulae or in preparation of samples for IR examination is recommended.

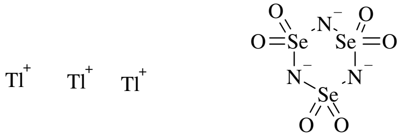
See Sodium tetrasulfur pentanitridate

See other N—S COMPOUNDS

See related NITRIDES

4756. Thallium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3-5-triide ('Thallium triselenimidate')

[ ] **$N_3O_6Se_3Tl_3$**



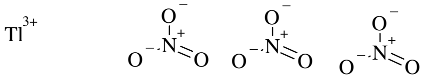
Explosive.

See Selenium difluoride dioxide: Ammonia

See other N-METAL DERIVATIVES

4757. Thallium(III) nitrate

[13746-98-0] **N_3O_9Tl**



Formic acid, 4-Hydroxy-3-methoxybenzaldehyde

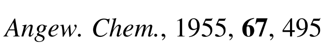
491M, 1975, 416

Addition of a little of the aldehyde (vanillin) to a strong solution of the trihydrated nitrate in 90% formic acid led to a violent (redox) reaction.

See other METAL NITRATES, REDOX REACTIONS

4758. Vanadium trinitrate oxide

[16017-37-1] **$N_3O_{10}V$**



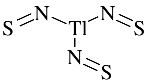
Organic materials

1. Schmeisser, M., *Angew. Chem.*, 1955, **67**, 495
2. Harris, A. D. *et al., Inorg. Synth.*, 1967, **9**, 87

Many hydrocarbons and organic solvents ignite on contact with this powerful oxidant and nitrating agent [1], which reacts like fuming nitric acid with paper, rubber or wood [2].

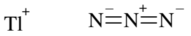
See other OXIDANTS
See related METAL NITRATES

4759. Tris(thionitrosyl)thallium
[ ] **N_3S_3Tl**



Bailar, 1973, Vol. 1, 1162
The compound and its adduct with ammonia explode very easily with heat or shock.
See other N-METAL DERIVATIVES, N—S COMPOUNDS

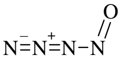
4760. Thallium(I) azide
[13847-66-0] **N_3Tl**



$Tl^+ \quad \overset{-}{N}{=}\overset{+}{N}{=}N^-$

Mellor, 1940, Vol. 8, 352
A relatively stable azide, it can be exploded on fairly heavy impact, or by heating at 350—400°C.
See other METAL AZIDES

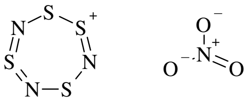
4761. Nitrosyl azide
[62316-46-5] **N_4O**



1. Lucien, H. W., *J. Amer. Chem. Soc.*, 1958, **80**, 4458
2. Klapötke, T. M., *et al., Angew. Chem. (Int.)*, 1993, **32**(11), 1610
3. Tornieporth-Oetting, I. C. *et al., Angewand. Chem. (Int.)*, 1995, **34**(5), 511

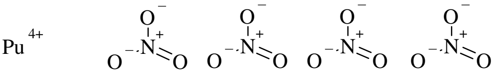
Explosions were experienced on several occasions during preparation of nitrosyl azide by various methods [1]. A yellow solid at —85°C, it decomposes even at —50°C [2]. It has an enthalpy of detonation of 6.3 kJ/g, the same as nitroglycerine, and a cavity volume greater than 600 ml in the lead block test (TNT = 300; Nitroglycerine = 520 ml) [3].
See other HIGH-NITROGEN COMPOUNDS, NON-METAL AZIDES

4762. Thiotrithiazyl nitrate
[79796-40-0] (ion) **$N_4O_3S_4$**



Goehring, 1957, 74
It explodes on friction or impact.
See other N—S COMPOUNDS

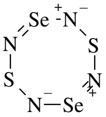
4763a. Plutonium(IV) nitrate
[13823-27-3] **$N_4O_{12}Pu$**



MCA Case History No. 1498

Polythene bottles are not suitable for long-term storage of plutonium nitrate solutions as radiation-induced stress cracks appeared in the bases of several 10 l bottles during 6 months' storage. Short-term storage and improved venting are recommended.
See Americium trichloride
See other IRRADIATION DECOMPOSITION INCIDENTS, METAL NITRATES

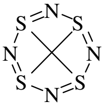
4763b. Diseleniumdisulfur tetranitride
[ ] **$N_4S_2Se_2$**



1. Maaninen, A. *et al., Phosphorus, Sulfur, Silicon Relat. Elem.*, 1997, (124-125), 457
2. Maaninen, A. *et al., Inorg. Chem.*, 1999, **38**(15), 3540

Like the homologues below, this compound is explosive on heating or mechanical stress [1]. It should be stored under hydrocarbons in quantities less than 1 gram [2].
See Tetraselenium tetranitride
See Tetrasulfur tetranitride
See Tritellurium tetranitride
See other NITRIDES, N—S COMPOUNDS

4764. Tetrasulfur tetranitride
[28950-34-7] **N_4S_4**



1. Mellor, 1940, Vol. 8, 625
2. Brauer, 1963, Vol. 1, 406
3. Villema-Blanco, M. *et al., Inorg. Synth.*, 1967, **9**, 101

4. Banister, A. J., *Inorg. Synth.*, 1977, **17**, 197—198
5. Witt, M. W. R. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 1668
6. Mark, H. *et al., Chem. Eng. News*, 1984, **62**(5), 4
7. Buntain, G. A., *Chem. Eng. News*, 1988, **66**(18), 2

The endothermic nitride is susceptible to explosive decomposition on friction, shock or heating above 100°C [1]. Explosion is violent if initiated by a detonator [2]. Sensitivity toward heat and shock increases with purity. Preparative precautions have been detailed [3], and further improvements in safety procedures and handling described [4]. An improved plasma pyrolysis procedure to produce poly(sulfur nitride) films has been described [5]. Light crushing of a small sample of impure material (m.p. below 160°C, supposedly of relatively low sensitivity) prior to purification by sublimation led to a violent explosion [6] and a restatement of the need [4] for adequate precautions. Explosive sensitivity tests have shown it to be more sensitive to impact and friction than is lead azide, used in detonators. Spark-sensitivity is, however, relatively low [7].

Metal chlorides

Roesky, H. W. *et al., Inorg. Chem.*, 1984, **23**, 75—76

The 1:1 complex with titanium chloride or the 1:2 complex with beryllium chloride may explode violently. Careful pyrolysis of these gives mixtures of disulfur dinitride and its 1:1 complexes with the metal chlorides, which may also explode, so screening is essential.

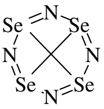
Oxidants

Pascal, 1956, Vol. 10, 645—646

Contact with fluorine leads to ignition, and interaction with metal chlorates or oxides is violent.

See other ENDOTHERMIC COMPOUNDS, NITRIDES, N—S COMPOUNDS

4765. Tetraselenium tetranitride
[10102-12-2] **N_4Se_4**



Alone, or Halogens and derivatives

1. Mellor, 1947, Vol. 10, 789
2. Kelly, P. F. *et al., Polyhedron*, 1990, **9**(13), 1567

The dry material explodes on slight compression, or on heating at 130—230°C. Contact with bromine, chlorine or a little fuming hydrochloric acid also causes explosion [1]. Explosions when manipulated with a metal spatula are reported [2].

See other NITRIDES

See related N—S COMPOUNDS

4766. Tritellurium tetranitride

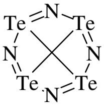
[ ] **N_4Te_3**

Structure unknown

Schmitz-Du Mont, O. *et al., Angew. Chem. (Int.)*, 1967, **6**, 1071
This yellow compound, prepared by ammonolysis of dipotassium triimidotellurite, was too explosive to be able to weigh it out for analysis.
See Tetratellurium tetranitride
See other NITRIDES

4767. Tetratellurium tetranitride

[12164-01-1] **N_4Te_4**



1. Fischer, F. *et al., Ber.*, 1910, **43**, 1472
2. Garcia-Fernandez, H., *Bull. Soc. Chim. Fr. [4]*, 1973, 1210—1215

The compound, previously formulated as tritellurium tetranitride is now shown to have the title structure (though probably polymeric, with inter-ring bonding). Two forms were originally described, one black which explodes on impact, and one yellow which explodes at 200°C [1]. It is explosive when dry, but may be stored safely under carbon tetrachloride [2].
See other NITRIDES
See related N—S COMPOUNDS

4768. Trithorium tetranitride

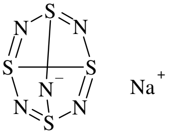
[12033-90-8] **N_4Th_3**

$Th^{4+}\quad Th^{4+}\quad Th^{4+}\quad N^{3-}\quad N^{3-}\quad N^{3-}\quad N^{3-}$

Air, or Oxygen
Mellor, 1940, Vol. 8, 122
It burns incandescently on heating in air, and very vividly in oxygen.
See other NITRIDES

4769. Sodium tetrasulfur pentanitridate

[60241-33-0] **N_5NaS_4**



Scherer, O. J. *et al., Angew. Chem. (Intern. Ed.)*, 1975, **14**, 485

It explodes at about 180°C, or under pressure, or by friction of a spatula on a sintered glass filter.
See other N-METAL DERIVATIVES, NITRIDES, N—S COMPOUNDS

4770. Triphosphorus pentanitride

[12136-91-3] **N_5P_3**

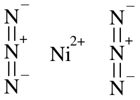
P_3N_5

Metals
Mellor, 1971, Vol. 8, Suppl. 3, 370—371
Interaction with molten magnesium at 651°C is explosive, and more so with calcium at 200°C.

Oxidants
Partington, 1946, 618
It ignites on heating in chlorine or oxygen.
See also ‘TETRAPHOSPHORUS HEXANITRIDE’
See other NITRIDES

4771. Nickel azide

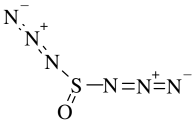
[59865-91-7] **N_6Ni**



Mellor, 1940, Vol. 8, 355
It explodes at 200°C.
See other METAL AZIDES

4772. Sulfinyl azide

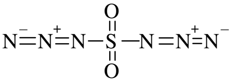
[ ] **N_6OS**



Pascal, 1961, Vol. 10, 634
An explosive liquid.
See other ACYL AZIDES, NON-METAL AZIDES

4773. Sulfuryl diazide

[72250-07-8] **N_6O_2S**



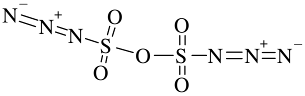
1. Curtius, T. *et al., Ber.*, 1922, **55**, 1571
2. Nojima, M., *J. Chem. Soc., Perkin Trans. 1*, 1979, 1813

It explodes violently when heated and often spontaneously at ambient temperature [1]. A safe method of preparation in solution has been described [2].

See other ACYL AZIDES, NON-METAL AZIDES

4774. Disulfuryl diazide

[73506-23-7] **$N_6O_5S_2$**



Alone, or Alkali

Lehmann, H. A. *et al., Z. Anorg. Chem.*, 1957, **293**, 314

The azide decomposes explosively below 80°C and should only be stored in 1 g quantities. In contact with dilute alkali at 0°C an explosive deposit is formed (? sodium azidosulfate?).

See other ACYL AZIDES, NON-METAL AZIDES

4775. 'Tetraphosphorus hexanitride'

[ ] **'N_6P_4'**

Unknown Structure

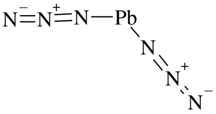
Mellor, 1971, 8, Suppl. 3, 371

Supposedly impure triphosphorus pentanitride, it ignites in air.

See related NITRIDES

4776. Lead(II) azide

[13424-46-9] **N_6Pb**



1. Mellor, 1940, Vol. 8, 353;, 1967, Vol. 8, Suppl. 2, 21, 50
2. Taylor, G. W. C. *et al., J. Crystal Growth*, 1968, **3**, 391
3. Barton, A. F. M. *et al., Chem. Rev.*, 1973, **73**, 138
4. *MCA Case History No. 2053*

As a heavy metal azide, it is rather endothermic (ΔH_f° (s) +436.4 kJ/mol, 1.50 kJ/g).

As a widely used detonator, its properties have been studied in great detail. Although quantitatively inferior to mercury fulminate as a detonator, it has proved to be more reliable in service. The pure compound occurs in 2 crystalline forms, one of which appears to be much more sensitive to initiation [1]. Factors which suppressed spontaneous explosions of lead azide during crystallisation were vigorous agitation and use of hydrophilic colloids [2]. These aspects have been reviewed [3]. A vacuum-desiccated sample of 5 g of the azide exploded violently when touched with a metal spatula [4] (possibly owing to static charge, generated by rapid evaporation of the solvent from the glass-insulated system, being earthed by the spatula).

See Sodium azide: Heavy metals (reference 1)

Calcium stearate

MCA Case History No. 949

An explosion occurred during blending and screening operations on a mixture of lead azide and 0.5% of calcium stearate. If free stearic acid were present as impurity in the calcium salt, free hydrogen azide may have been involved.

Copper, or Zinc

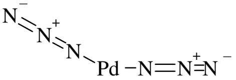
Federoff, 1960, A532, 551

Lead azide, on prolonged contact with copper, zinc or their alloys, forms traces of the extremely sensitive copper or zinc azides which may initiate detonation of the whole mass of azide.

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

4777. Palladium(II) azide

[13718-25-7] **N_6Pd**



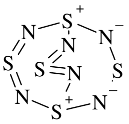
Ukhin, L. Yu. *et al., J. Organomet. Chem.*, 1981, **210**, 270

The explosive precipitate needs careful handling.

See other METAL AZIDES

4778. Pentasulfur hexanitride

[68993-02-2] **N_6S_5**



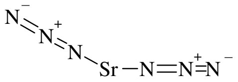
Sheldrick, W. S. *et al., Inorg. Chem.*, 1980, **19**, 539

Powerfully explosive, like its dimethyl homologue. A m.p. apparatus was wrecked, and a large glass funnel containing 50 mg was pulverised.

See other NITRIDES, N—S COMPOUNDS

4779. Strontium azide

[19465-89-5] **N_6Sr**



It is somewhat endothermic (ΔH_f° (s) +204.6 kJ/mol, 1.19 kJ/g).

See Barium azide

See also Calcium azide

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

4780. Zinc azide

[14215-28-2] **N_6Zn**

$N\overset{-}{=}N\overset{+}{=}N—Zn—N=N\overset{+}{=}N^-$

Bailar, 1973, Vol. 3, 217

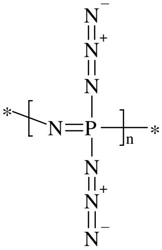
Zinc azide is said to explode easily.

See SODIUM AZIDE: HEAVY METALS

See other METAL AZIDES

4781. Poly(diazidophosphazene)

[ ] **$(N_7P)_n$**



Dillon, K. B. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 1037

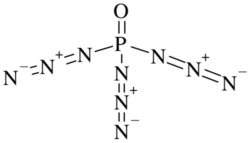
This polymer of phosphonitrilic diazide is a viscous explosive oil.

See 1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine

See other NON-METAL AZIDES

4782. Phosphorus triazide oxide

[4635-46-5] **N_9OP**



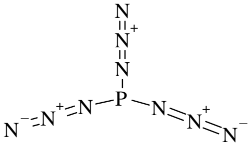
Buder, W. *et al., Z. Anorg. Chem.*, 1975, **415**, 263

The liquid may explode violently on warming from 0°C to ambient temperature, but can be used safely in solution.

See related ENDOTHERMIC COMPOUNDS, NON-METAL AZIDES

4783. Phosphorus triazide

[56280-76-3] **N_9P**



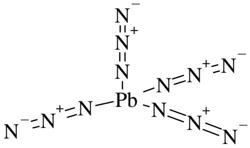
1. Lines, E. L. *et al., Inorg. Chem.*, 1972, **11**, 2270
2. Buder, W. *et al., Z. Anorg. Chem.*, 1975, **415**, 263

It is a highly explosive liquid [1], which may explode on warming from 0°C to ambient temperature, but can be used safely in solution [2].

See other NON-METAL AZIDES

4784. Lead(IV) azide

[73513-16-3] **$N_{12}Pb$**



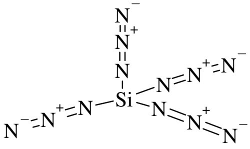
1. Mellor, 1967, Vol. 8, Suppl. 2, 22
2. Möller, H., *Z. Anorg. Chem.*, 1949, **260**, 10
3. Zbirol, E., *Synthesis*, 1972, (6), 285—302

The crystalline product appears less stable than the diazide, spontaneously decomposing, sometimes explosively [1]. It was rated as too unstable for use as a practical detonator or explosive [2]. Lead(IV) acetate azide (probably the triacetate azide) is also rather unstable, evolving nitrogen above 0°C with precipitation of lead(II) azide [3]. Lead(IV) azide will be considerably more endothermic than the lead(II) salt.

See other ENDOTHERMIC COMPOUNDS, METAL AZIDES

4785a. Silicon tetraazide

[27890-58-0] **$N_{12}Si$**



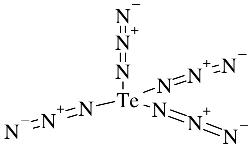
1. Mellor, 1967, Vol. 8, Suppl. 2, 20
2. Wiberg, E. *et al., Z. Naturforsch. B*, 1954, **9B**, 500
3. Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 27

Spontaneous explosions have been observed [1] with this dangerously explosive material, especially when pure. A sample at 0°C exploded during removal of traces of benzene under high vacuum [2]. A residue containing the tetraazide, silicon chloride triazide and probably silicon dichloride diazide, exploded on standing for 2 or 3 days, possibly owing to hydrazoic acid produced by hydrolysis.

See other ENDOTHERMIC COMPOUNDS, NON-METAL AZIDES

4785b. Tellurium tetraazide

[656253-42-8] **$N_{12}Te$**



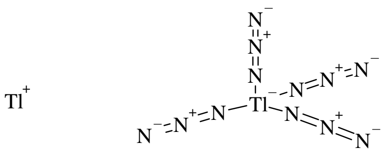
1. Klapötke, T. M. *et al., Angew. Chem. (Int.)*, 2003, **42**(47), 5843
2. Haiges, R. *et al., Angew. Chem. (Int.)*, 2003, **42**(47), 5847

The preparation of this extremely explosive material is reported, It once exploded spontaneously on isolation. It is recommended that no more than 100 mg be handled, using face-shields, leather aprons, Kevlar gloves and Teflon spatulas. Some pentaazidotellurate(IV) salts were also prepared; a yellow oil probably the crude tetramethylammonium salt exploded on stirring [1]. Tellurium tetraazide was reported by another group at much the same time, they also prepared a hexaazido-tellurate (2-) as the bis(tetraphenylphosphonium) salt [2].

See other NON-METAL AZIDES

4786. Thallium(I) tetraazidothallate

[ ] **$N_{12}Tl_2$**



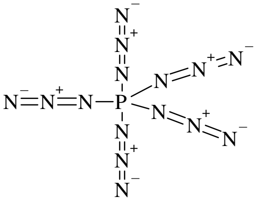
Bailar, 1973, Vol. 1, 1152

A heat-, friction- and shock-sensitive explosive.

See related ENDOTHERMIC COMPOUNDS, HEAVY METAL DERIVATIVES, METAL AZIDES

4787a. Pentaazidophosphorane (Phosphorus pentaazide)

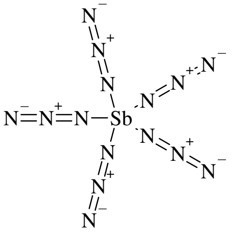
[56295-87-5] **$N_{15}P$**



See Sodium hexaazidophosphate, below

4787b. Antimony pentaazide

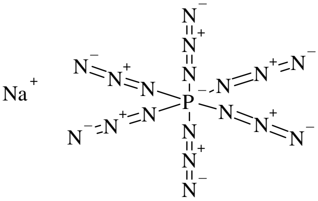
[364329-90-8] **$N_{15}Sb$**



See Arsenic pentaazide

4788. Sodium hexaazidophosphate

[60955-41-1] **$N_{18}NaP$**



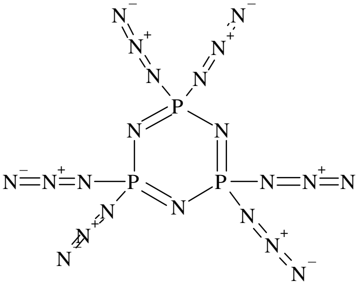
1. Volgnandt, P. *et al., Z. Anorg. Chem.*, 1976, **425**, 189—192
2. Buder, W. *et al., Z. Anorg. Chem.*, 1975, **415**, 263

The product of interaction of sodium azide and phosphorus trichloride occasionally exploded on warming from 0°C to ambient temperature, but was examined safely in solution. The structure of the explosive product is determined as the title compound [1], rather than pentaazidophosphorane as originally reported [2]. It contains some 82% of nitrogen.

See other ENDOTHERMIC COMPOUNDS, HIGH-NITROGEN COMPOUNDS

See related NON-METAL AZIDES

4789. 1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine
[22295-99-4] **$N_{21}P_3$**



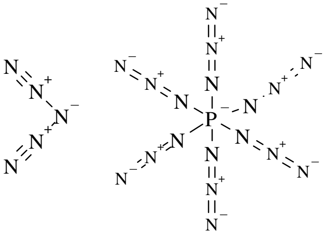
1. Grundmann, C., *Z. Naturforsch. B*, 1955, **10B**, 116
2. Tornieporth-Oetting, I. C. *et al., Angewand. Chem. (Int.)*, 1995, **34**(5), 511

This viscous liquid (containing 73.5% N) is violently explosive when subjected to shock, friction [1] or electric discharge [2].

See Poly(diazidophosphazene)

See other ENDOTHERMIC COMPOUNDS, HIGH-NITROGEN COMPOUNDS, NON-METAL AZIDES

4789b. N_5(1+) hexaazidophosphate (Pentazonium hexaazidophosphate)
[ ] **$N_{23}P$**



Haiges, R. *et al., Angewand. (Int.)*, 2004, **43**(37), 4919

A white 'marginally stable', very shock sensitive solid, disposing of 6.8 kJ/g (calculated), 92% nitrogen. Millimolar quantities can do serious damage, handle less than 2 mmol. Heavy personal protection – screens, visor, leather apron, Kevlar gloves is recommended, as is use of (non-shattering and blunt sharded) Teflon apparatus. Since N_5^+ is a powerful oxidant, it is sensitised by fuels such as polythene. The tetraazidoborate is similar, but slightly less energetic.

See other HIGH-NITROGEN COMPOUNDS, INORGANIC AZIDES

4790. Sodium
[7440-23-5] **Na**

Na

(*MCA SD-47*, 1952); *NSC 231*, 1978; *FPA H4*, 1972; *HCS 1980*, 823

1. Hawkes, A. S. *et al., J. Chem. Educ.*, 1953, **30**, 467
2. *Alkali Metals*, 1957
3. Houben-Weyl, 1979, Vol. 13.1, 287—289
4. Muir, G. D., private comm., 1968
5. Reuillon, M. *et al., Proc. 2nd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 481—486, Frankfurt, Dechema, 1978
6. Anon., *Fire Prevention*, 1995, (May), 39

In a discussion of safe methods for laboratory use of sodium, disposal of small quantities (up to 5—10 g) by immersion in isopropanol, which may contain up to 2% of water to increase the rate of reaction, is recommended. Quantities up to 50 g should be burned in a heavy metal dish, using a gas flame [1], (with suitable arrangements for dispersion or absorption of the alkaline particulate smoke so produced). Handling techniques and safety precautions for large-scale operations have also been detailed for this reactive metal [2]. Techniques for the preparation and precautions in use of finely dispersed sodium ('sodium sand') are given. It is to some extent pyrophoric [3]. Dispersions of sodium in volatile solvents may become pyrophoric if the solvent evaporates round the neck of a container. Serum cap closures are safer than screw caps [4]. Improved methods for extinction of liquid sodium (and other metal) fires are described which involve application of low-melting inorganic powder mixtures which melt and form a protective crust. Mixtures of sodium carbonate or graphite, with lithium carbonate, sodium chloride or sodium fluoride are very effective for sodium [5]. A fire involving a leak of bulk liquid sodium, which ignited, is reported. Autoignition in air can be as low as 100°C [6].

Acids MRH values below reference

Mellor, 1941, Vol. 2, 469—470

MRH Hydrogen chloride 5.36/61, hydrogen fluoride 6.95/47, nitric acid 5.48/64, sulfuric acid 3.89/69

Anhydrous hydrogen chloride, hydrogen fluoride or sulfuric acid react slowly with sodium, while the aqueous solutions react explosively. Nitric acid of density above 1.056 causes ignition of sodium.

Ammonia, 1,2-Dimethoxyethane, Pyridine

Nolan, 1983, Case history 215

Pyridine is converted to a slurry of a dihydrobipyridyl by treatment with sodium in liquid ammonia at —33°C, then warming to 10°C to evaporate excess ammonia. The slurry was then transferred to a decomposition vessel (for subsequent aerobic oxidation to liberate bipyridyl), the transfer pipe being flushed through with cold dimethoxyethane. When warm solvent was used for this purpose on one occasion, oxidation proceeded so fast that ignition occurred.

Ammonia, Aromatic hydrocarbons

Stevenson, J. R. *et al., J. Org. Chem.*, 1984, **49**, 3444

When naphthalene is reduced in liquid ammonia by metallic potassium, evaporation of excess ammonia gives the solvated solid potassium naphthalide ($K_2 . NH_3 . Naphth_2$). If sodium is used in place of potassium, the product detonates as crystallisation starts. This is attributed to energetic expulsion of ammonia held endothermically in the growing crystal lattice. The same also occurs with anthracene and sodium, and nitrobenzene and barium. Caution in preparing and using these compounds is urged.

Aqua Regia
See AQUA REGIA: Sodium

Calcium, Mixed oxides
See Calcium: Sodium, etc.

Chlorobenzene, Phosphorus trichloride
Venczel, A., Rom. Pat. RO 72 608, 1980
In the preparation of triphenylphosphine from chlorobenzene, phosphorus trichloride and sodium dispersed in toluene or xylene, the possibility of explosion is avoided by adding about 1 mol% of a lower alcohol, based on sodium usage.

1-Chlorobutane, Light petroleum
Shackelford, S. A., *J. Org. Chem.*, 1979, **44**, 3492, footnote 30
In formation of butylsodium, the temperature of interaction of the chloro compound with the dispersion of sodium in light petroleum must not be too low. At —23°C, reaction is smooth, but at —78° excess of chlorobutane accumulated, and when reaction did start, it accelerated to violent explosion.
See Halocarbons (reference 7), below

Chloroform, Methanol
See Chloroform: Sodium, Methanol

Diazomethane
See Diazomethane: Alkali metals

Diethyl ether
Hey, P., private comm., 1965
While sodium wire was being pressed into ether, the die-hole blocked. Increasing the pressure on the ram to free it caused ignition of the ejected sodium and explosion of the flask of ether. Pressing the sodium into less flammable xylene or toluene and subsequent replacement of solvent with ether was recommended.

Dimethylformamide
‘DMF Brochure’, Billingham, ICI, 1965
A vigorous reaction occurs on heating DMF with sodium metal.

Ethanol
Brändstrom, A., *Acta Chem. Scand.*, 1951, **4**, 1608—1610
Air must be excluded during exothermic interaction of ethanol with sodium finely dispersed in hydrocarbons to avoid the possibility of hydrogen—air mixture explosions.
See Potassium: Alcohols

Fluorinated alkanols
1. Anon., personal communication, 1996
2. Editor’s comments

By mistake, sodium was added to excess liquid perfluoroalkylmethanol in the absence of the diluent which had previously moderated the reaction. Vigorous initial reaction culminated in an explosion which destroyed the flask and attached glassware and cracked the fume cupboard window, this was attributed to ignition of evolved hydrogen [1]. Since air would rapidly be swept from the flask by the gas flow, it seems probable that a hydrogen explosion sufficient to damage the hood would be external to the reaction flask. The desired fluoroalkoxide is undoubtedly thermodynamically unstable with respect to sodium fluoride formation and a number of other metal derivatives of fluorinated organics have proved explosively metastable [2].
See METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

Fluorinated compounds
Herring, D. E., private comm., 1964
Fusion of fluorinated compounds with sodium for qualitative analysis requires a high temperature for reaction because of their unreactivity. When reaction does occur, there is often an explosion and precautions must be taken.

Halocarbons MRH values below references

1. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
2. Lenze, F. *et al., Chem. Ztg.*, 1932, **56**, 921
3. Ward, E. R., *Proc. Chem. Soc.*, 1963, 15
4. *MCA SD-34*, 1949
5. Rayner, P. N. G., private comm., 1968
6. Anon., *Angew. Chem. (Nachr.)*, 1970, **18**, 397
7. Read, R. R. *et al., Org. Synth.*, 1955, Coll. Vol. 3, 158
8. Houben-Weyl, 1970, Vol. 13.1, 394—395
9. Firat, Y., *Makromol. Chem.*, 1975, Suppl. 1, 207
10. Grattan, D. W. *et al., J. Chem. Soc., Dalton Trans.*, 1977, 1734—1744

MRH Carbon tetrachloride 6.10/63, chloroform 5.82/63, 1,2-dichloroethylene 5.52/68, trichloroethylene 5.94/66

Although apparently stable standing in contact, mixtures of sodium with a range of halogenated alkane solvents are metastable and capable of initiation to explosion by shock or impact. Carbon tetrachloride [1,2,3], chloroform, dichloromethane and chloromethane [1,2], tetrachloroethane [1,2,4] have been investigated, among others. Generally the sensitivity to initiation and the force of the explosion increase with the degree of halogen substitution; the two former less than in the corresponding systems with potassium or potassium—sodium alloy. Any aliphatic halocarbon (except fully fluorinated alkanes) may be expected to behave in this way. Small portions of sodium and hexachlorocyclopentadiene were mixed in preparation for a sodium fusion test. On shaking a few min later, the tube exploded [5].

On the small scale, no reaction occurred on boiling perfluorohexyl iodide in contact with metallic sodium. With 140 g of iodide and 7 g of sodium an explosion occurred after 30 min [6]. The temperature range for smooth interaction of bromobenzene, 1-bromobutane and sodium in ether to give butylbenzene is critical. Below 15°C reaction is delayed but later becomes vigorous, and above 30°C the reaction becomes violent [7]. Sodium wire and chlorobenzene react exothermally in benzene under nitrogen to give phenylsodium, and the reaction must be controlled by cooling. Use of

finely divided sodium will lead to an uncontrollable, explosive reaction [8]. The hazards of contacting dichloromethane with a sodium film during an ultra-drying procedure are stressed. Thorough pre-drying and operations under vacuum are essential precautions [9]. Purification of chloromethane, chloroethane, or dichloromethane by condensation onto a fresh sodium mirror is extremely dangerous unless the halocarbons are very dry and oxygen-free [10].
See Chlorobenzene, etc.
See 1-Chlorobutane
See Chloroform, etc.
See Chloroform: Metals
See Iodomethane: Sodium
See Lithium: Bromobenzene
See entry METAL—HALOCARBON INCIDENTS

Halogen azides
See HALOGEN AZIDES: Metals

Halogens, or Interhalogens MRH Chlorine 6.90/61, Fluorine 13.43/45

1. Mellor, 1961, Vol. 2, Suppl. 2.1, 450—452
2. Mellor, 1941, Vol. 2, 114, 469
3. Mellor, 1941, Vol. 2, 92, 469
4. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
5. Booth, H. S. *et al., Chem. Rev.*, 1947, **41**, 427
6. Pascal, 1966, Vol. 2.1, 221

Sodium ignites in fluorine gas but is inert in the liquefied gas [1]. Cold sodium ignites in moist chlorine [2] but may be distilled unchanged in the dry gas [1]. Sodium and liquid bromine appear to be unreactive on prolonged contact [3], but mixtures may be detonated violently by mechanical shock [4]. Finely divided sodium luminesces in bromine vapour [1]. Iodine bromide or iodine chloride react slowly with sodium, but mixtures will explode under a hammer-blow [1]. Interaction of iodine pentafluoride with solid sodium is initially vigorous, but soon slows with film-formation, while that with molten sodium is explosively violent [2]. Sodium reacts immediately and incandescently with iodine heptafluoride [5]. Mixtures of solid sodium and iodine explode lightly when initiated by shock [6].

Hydrazine
Mellor, 1940, Vol. 8, 316
Anhydrous hydrazine and sodium react in ether to form sodium hydrazide, which explodes in contact with air. Hydrazine hydrate and sodium react very exothermally, generating hydrogen and ammonia.

Hydroxylamine MRH 3.85/99+
See Hydroxylamine: Metals

Iodates
Cueilleron, J., *Bull. Soc. Chim. Fr.*, 1945, **12**, 88—89
Mixtures of sodium with silver iodate or sodium iodate explode when initiated by shock.

See Oxidants, below

Mercury

Brauer, 1965, Vol. 2, 1802

Interaction of sodium and mercury to form sodium amalgam is violently exothermic, and moderation of the reaction with an inert liquid, or by adding mercury slowly to the sodium is necessary. Even so, temperatures of 400°C may be attained.

Metal halides

MRH Ammonium chloride 2.64/66, iron(III) chloride, 3.60/70, manganese(II) chloride 1.97/73, tin(II) chloride 1.38/84, vanadium(III) chloride 2.38/83, vanadyl chloride 2.30/82

1. *Alkali Metals*, 1957, 129
2. Mellor, 1961, Vol. 2, Suppl. 2.1, 494—496
3. Staudinger, H., *Z. Elektrochem.*, 1925, **31**, 549
4. Cueilleron, J., *Bull. Soc. Chim. Fr.*, 1945, **12**, 88

Sodium dispersions will reduce many metal halides exothermically. Iron(III) chloride is reduced fairly smoothly at ambient temperature or below in presence of 1,2-dimethoxyethane. Nickel chloride, cobalt chloride, lead chloride or calcium chloride require higher temperatures to initiate the reaction, the exotherm with cobalt chloride increasing the temperature from 325 to 375°C and causing evaporation of most of the dispersing oil [1]. The finely powdered metals produced by reduction of halides of cadmium, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, silver, tin or zinc with sodium dispersed in ether or toluene, are all pyrophoric [2]. Interaction of sodium with vanadyl chloride at 180°C is violent [2]. Mixtures of sodium with metal halides are sensitive to mechanical shock [3]; the ensuing explosions have been graded for intensity. Very violent explosions occurred with iron(III) chloride, iron(III) bromide, iron(II) bromide, iron(II) iodide, cobalt(II) chloride or cobalt(II) bromide. Strong explosions occurred with the various halides of aluminium, antimony, arsenic, bismuth, copper(II), mercury, silver, and tin (including a mixture of tin(IV) iodide and sulfur), also vanadium(V) chloride and ammonium tetrachlorocuprate. Ammonium, copper(I), cadmium and nickel halides generally gave weak explosions, and most of the alkali- and alkaline earth-metals were insensitive [4].

See Molybdenum pentachloride: Sodium, or Sodium sulfide

See Tungsten hexachloride: Sodium sulfide

Metal oxides

MRH Chromium trioxide 3.39/79, copper(II) oxide 2.05/63, sodium peroxide 2.55/63, vanadium(V) oxide 1.30/84

1. Mellor, 1939, Vol. 9, 649
2. Mellor, 1943, Vol. 11, 237, 542
3. Mellor, 1941, Vol. 3, 138
4. Mellor, 1941, Vol. 7, 658, 401
5. Mellor, 1940, Vol. 4, 770
6. Brewer, L. *et al., Rept. UCRL 1864*, 7, Washington, USAEC, 1952
7. Mellor, 1961, Vol. 2, Suppl. 2.1, 474

Bismuth(III) oxide[1], chromium trioxide [2], and copper(II) oxide [3], are reduced with incandescence on heating with sodium. Finely divided sodium ignites on admixture with fine lead oxide without heating, while the coarse material reacts vigorously with molten sodium [4]. The latter reduces mercury(I) oxide [5] or molybdenum trioxide [2] with incandescence, the former producing a light explosion also. Sodium reduces sodium peroxide vigorously at 500°C [6] and tin(IV) oxide incandescently on gentle heating [4]. Finely dispersed sodium reduces metal oxides on heating at temperatures between 100 and 300°C, producing, e.g., pyrophoric iron, nickel and zinc [4].

Nitrogen-containing explosives

Leleu, *Cahiers*, 1975, (79), 266

Mixtures of sodium (or its alloy with potassium) and nitromethane, trichloronitromethane, nitrobenzene, dinitrobenzene, dinitronaphthalene, ethyl nitrite, ethyl nitrate or glyceryl nitrate are shock-sensitive, the sensitivity increasing with the number of nitro groups.

Non-metal halides MRH values below references

1. Mellor, 1940, Vol. 8, 1033
2. Mellor, 1941, Vol. 2, 470
3. Mellor, 1940, Vol. 8, 1016
4. Mellor, 1961, Vol. 2, Suppl. 2.1, 455, 460
5. Mellor, 1940, Vol. 8, 1073
6. Cueilleron, J., *Bull. Soc. Chem. Fr.*, 1945, **12**, 88
7. Mellor, 1947, Vol. 10, 912
8. Kirk-Othmer, 1969, Vol. 18, 438
9. Leleu, *Cahiers*, 1975, (79), 270

MRH Phosphorus trichloride 3.10/67, phosphorus pentachloride 4.89/65, phosphoryl chloride 4.27/69, sulfinyl chloride 5.27/67

Sodium floats virtually unchanged on phosphorus tribromide, but added drops of water caused a violent explosion [1]. Molten sodium explodes with phosphorus trichloride [2] and may ignite or explode with phosphorus pentachloride [3]. Diselenium dichloride reacts vigorously with sodium on heating, emitting light and heat [4]. Sodium ignites in sulfinyl chloride vapour at 300°C [4], or in a stream of thiophosphoryl fluoride [5]. The shock-sensitive mixtures of sodium with phosphorus pentachloride, phosphorus tribromide or sulfur dichloride gave violent explosions on impact, while those with boron tribromide or sulfur dibromide gave strong explosions [6]. Sodium and phosphoryl chloride interact explosively on heating [8], and mixtures of sodium with sulfinyl fluoride or silicon tetrachloride or silicon tetrafluoride are shock-sensitive explosives [9].

Non-metal oxides MRH values below references

1. Mellor, 1940, Vol. 6, 70; 1961, Vol. 2, Suppl. 2.1, 468
2. Gilbert, H. N., *Chem. Eng. News*, 1948, **26**, 2604
3. Mellor, 1940, Vol. 8, 554, 945; 1961, Vol. 2, Suppl. 2.1, 458
4. Leleu, *Cahiers*, 1975, (79), 269
5. Weiss, E., *Angew. Chem. (Int.)*, 1993, **32**(11), 1518

MRH Carbon monoxide 6.15/65, chlorine dioxide 5.69/75, sulfur dioxide 4.56/74, sulfur trioxide 5.06/70

Sodium and carbon dioxide are normally unreactive till red-heat has been attained [1], but mixtures of the 2 solids are impact-sensitive and explode violently [2]. Carbon dioxide is unsuitable as an extinguishant for the burning metal alone, as the intensity of combustion is increased by replacing air with carbon dioxide (72.7% oxygen content). However it has been used successfully to extinguish solvent fires where sodium was also present, since it often fails to ignite because of the blanketing effect of solvent vapour. Conversely addition of kerosene to burning sodium enables the whole to be extinguished with carbon dioxide [1]. Finely divided silica (sand) will often react with burning sodium, so is not entirely suitable as an extinguishant [1,2]. (Anhydrous sodium carbonate and sodium chloride are suitably unreactive for this purpose.) Solid sodium is inert to dry liquid or gaseous sulfur dioxide, but molten sodium reacts violently [2]. The moist gas reacts almost as vigorously as water [1]. Phosphorus pentaoxide becomes incandescent on warming with sodium, which also ignites in dinitrogen pentaoxide [3]. The product of interaction of carbon monoxide with sodium (not sodium carbonyl as previously thought [2], but the hexamer), sodium benzenehexoxide, is shock sensitive, explodes at 90°C and contact with water causes explosion or ignition to occur [4]. Later work [5] makes it likely that this compound is, in fact, the dimer disodium ethynediolate.

Non-metals MRH Sulfur 4.81/41

1. Mellor, 1961, Vol. 2, Suppl. 2.1, 466—467, 454—455
2. Mellor, 1941, Vol. 2, 469
3. Mellor, 1947, Vol. 10, 766

Explosions have occasionally occurred when carbon powder is in contact with evaporating sodium and air [1]. The violent interaction of ground or heated mixtures of sodium and sulfur may be moderated by the presence of sodium chloride or boiling toluene [1,2]. Selenium reacts incandescently with sodium when heated [3], and molten tellurium reacts vigorously when poured on to solid sodium [1].

Organic samples for qualitative analysis

See LASSAIGNE TEST

Other reactants

Yoshida, 1980, 262—263

MRH values calculated for 19 combinations with various materials are given.

Oxidants MRH values show % of oxidant

See Ammonium nitrate: Metals MRH 4.15/64

See Halogens or Interhalogens; Metal halides;

See Metal oxides; Non-metal oxides, all above

See Nitric acid: Metals MRH 5.84/32

See Nitrosyl fluoride: Sodium

See Nitryl fluoride: Metals

See Sodium nitrate: Sodium MRH 3.85/43

See Sodium nitrite: Reducants MRH 3.42/50

See Sodium peroxide: Metals MRH 2.55/63

Oxygenated compounds

Leleu, *Cahiers*, 1975, (79), 267

Mixtures of inorganic oxygenated compounds (halide oxides or oxide sulfides) or oxygen-rich organic compounds (alkyl oxalates) with sodium (or its alloy with potassium) are shock-sensitive explosives.

See Non-metal oxides, above

Sulfides

Leleu, *Cahiers*, 1975, (79), 268, 270

Passage of moist hydrogen sulfide over unheated sodium causes melting and then usually ignition of the metal. Mixtures of sodium (or its alloy with potassium) and carbon disulfide are shock-sensitive explosives.

Sulfur

Hames, D. *et al., Proc. Inst. Electr. Eng.*, 1979, **126**, 1157—1161

Safety aspects of large arrays of sodium—sulfur batteries for rail traction are considered among technical aspects.

2,2,3,3-Tetrafluoropropanol

See 2,2,3,3-Tetrafluoropropanol: Potassium hydroxide, etc.

Tetrahydrofuran, Water

Anon., *Lab. Accid. Higher Educ.*, item 5, Barking, HSE, 1987

THF was being dried by refluxing over metallic sodium, and after the reflux period, heat was turned off and a stopper was put in the top of the condenser. The presence of the stopper was forgotten, and when heating was restarted, the condenser was ejected from the flask and broke. Escaping water came into contact with the sodium, evolving hydrogen which ignited and then set fire to the escaping THF vapour in a fume cupboard, and an explosion ensued.

See Water, below

Toluene

See Xylene, below

Water

1. Mellor, 1941, Vol. 2, 469
2. Mellor, 1961, Vol. 2, Suppl. 2.1, 362
3. *MCA Case History No. 456*
4. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633—636
5. *MCA Case History No. 1653*
6. *MCA Case History No. 2082*
7. Peacocke, T. A. H., *Chem. Brit.*, 1979, **15**, 233

Small pieces of sodium in contact with water react vigorously but do not usually ignite the evolved hydrogen unless the water is above 40°C, or if rapid dissipation of heat is prevented by immobilising the sodium by use of a viscous aqueous solution (starch paste, etc.) or wet filter paper [1]. In contact with ice, sodium explodes violently [2]. Small, hot particles of sodium (remaining from dissolution of larger pieces) may finally explode as do large lumps of the metal in water [1]. Sodium residues from a Wurtz reaction were treated with alcohol to destroy sodium, but later accidental contact with water caused a fire, showing that the alcohol treatment was incomplete. This may have been owing to a crust of alcohol-insoluble halide over the residual sodium [3]. Reactivity of sodium and other alkali-metals with water or steam has been discussed in detail [4]. Rolling a drum containing a 12 cm layer of sodium sludge mixed with soda ash led to a mild pressure explosion. Moisture present in the drum contacted the sodium residue when rolled [5]. Preparing to dispose of a few litres of old sodium dispersion by adding a solvent and then burning it, an operator opened the container under cover but in an atmosphere rendered humid by very recent rain. The dispersion immediately ignited and exploded [6]. An explosion of a small piece of sodium retained under water (out of contact with air) was attributed to formation of organic peroxides from arylsodium derivatives produced in storage of sodium under naphtha [7].

Xylene

Anon., *Sichere Chemiearb.*, 1989, **41**(5), 58

After storage for 16 years in a tin, a sealed bottle originally holding sodium dispersed in xylene was found to contain a yellow/white solid layer in place of the expected supernatant xylene. Scraping the solid out caused a violent explosion. The force of the explosion leads to a suspicion of peroxide formation, but there is no obvious explanation. Reactive materials like alkali-metal dispersions in volatile solvents should not be stored indefinitely, but clearly labeled after receipt or preparation to show the disposal date. Disposal of such dispersions by burning is recommended. Sodium dispersed in toluene might behave in the same way.

See ALKALI METALS

See other METALS

4791. Sodium—antimony alloy

[12300-03-7] (1:1 alloy) **Na—Sb**

Na—Sb

See Nitrosyl tribromide: Sodium—antimony alloy

See other ALLOYS

4792. Sodium—zinc alloy

[39422-73-6] (1:6 alloy) **Na—Zn**

Na—Zn

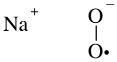
Houben-Weyl, 1973, Vol. 13.2a, 571

Preparation by addition of sodium to molten zinc (1:4) in absence of air is rather violent.

See other ALLOYS

4793. Sodium dioxide (Sodium superoxide)

[12034-12-7] **NaO_2**



$Na^+ \quad O^- - O\cdot$

Sodium peroxide

Gausing, W. *et al., Angew. Chem. (Intern. Ed.)*, 1978, **17**, 372

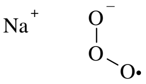
A by-product mixture of sodium dioxide and sodium peroxide separated by filtration was sensitive to warmth and shock when dry.

See other METAL OXIDES

See related METAL PEROXIDES, OXIDANTS

4794. Sodium trioxide

[12058-54-7] **NaO_3**



Petrocelli, A. W. *et al., J. Chem. Educ.*, 1962, **39**, 557

This is the least stable of the alkali-metal ozonides.

See other METAL OXIDES

See related METAL PEROXIDES, OXIDANTS

4795. Sodium silicide

[12164-12-4] **NaSi**

Na—Si

1. Mellor, 1961, Vol. 2, Suppl. 2.1, 564
2. Bailar, 1973, Vol. 1, 446

Sodium silicide ignites in air [1], and like its potassium, rubidium and caesium analogues, ignites explosively on contact with water or dilute acids [2].

See other METAL NON-METALLIDES

4796. Sodium oxide

[1313-59-3] **Na_2O**

$Na^+ \quad Na^+ \quad O^{2-}$

2,4-Dinitrotoluene

See 2,4-Dinitrotoluene: Sodium oxide

Phosphorus(V) oxide

See Tetraphosphorus decaoxide: Inorganic bases

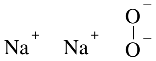
Water

Interaction is likely to be violently exothermic.

See other INORGANIC BASES, METAL OXIDES

4797. Sodium peroxide

[1313-60-6] **Na_2O_2**



$Na^+ \quad Na^+ \quad {}^-O{-}O^-$

FPA H104, 1981; *HCS 1980*, 854

1. Allen, C. F. H. *et al., J. Chem. Educ.*, 1942, **19**, 72
2. Rüst, 1948, 297

Hazards attendant on the use of this powerful oxidant may in many cases be eliminated by substitution with ‘sodium perborate’ (actually sodium borate hydrogen peroxidate) [1]. One of several wooden boxes of the peroxide (not clearly labelled as such) exploded with great violence during handling operations. It seems likely that contamination with a combustible material, or possibly with moisture, had occurred [2].

See Fibrous materials

See also Wood, below

Acetic acid MRH 2.80/16

von Schwartz, 1918, 321

Admixture causes explosion, owing either to direct oxidation of acetic acid by the highly concentrated hydrogen peroxide produced, or perhaps to formation of concentrated peroxyacetic acid.

Aluminium chloride MRH 2.30/53

Anon., *Chem. Eng. News*, 1954, **32**, 258

A mixture of the three slowly reacted, creating a pressure of 122 bar (? of chlorine and possibly hydrogen chloride) in 41 days, and the residue reacted spontaneously on exposure to air.

See Metals, etc., below

Aluminium, MRH 4.56/19

Ammonium peroxodisulfate MRH 2.72/60

Mellor, 1947, Vol. 10, 464

A mixture exploded on being subjected to friction in a mortar, heating above 75°C, or exposure to carbon dioxide or drops of water.

Boron nitride

Mellor, 1940, Vol. 8, 111

Addition of powdered nitride to the molten peroxide caused incandescence.

Calcium acetylide MRH 3.01/14

Mellor, 1941, Vol. 2, 490

A mixture is explosive.

Carbon dioxide, MRH 1.84/36

Charcoal MRH 3.05/7

Mellor, 1941, Vol. 3, 401

An intimate mixture ignites after a short delay (but the same is probably true if silver chloride is omitted).

See Non-metals, above

Cotton wool MRH Cellulose 1.97/99+

1. Bulavin, Yu. I., *Chem. Abs.*, 1978, **89**, 75003
2. Anon., *Chemist-Analyst*, 1978, **67**(3), 7

Cotton wool sprinkled with the peroxide (used in guard tubes) will ignite a few s after exposure to moist carbon dioxide. Exothermic interaction of sodium peroxide and carbon dioxide heats the cotton which then ignites in the liberated oxygen [1]. Cotton contaminated with peroxide should not be stored under any circumstances as it may ignite with atmospheric carbon dioxide [2].

Fibrous materials, Water MRH Cellulose 1.97/99+

1. von Schwartz, 1918, 328
2. Betteridge, D., private comm., 1973

Contact of the solid peroxide with moist cloth, paper or wood often causes ignition [1], and addition of water to intermixed cotton wool and peroxide causes violent ignition [2].

Glucose, Potassium nitrate MRH 2.93/15

491M, 1975, 391

A micro-bomb calorimeter exploded when the wrong proportions of sample and oxidants were used. Instead of 4 g of peroxide and 0.2 g of nitrate for 0.2 g of the sugar sample, 0.35 g of peroxide and 2.6 g of dextrose were used. The deficiency of peroxide to absorb the decomposition gases and excess of organic matter led to a rapid rise in temperature and pressure, which burst the bomb calorimeter.

Hexamethylenetetramine MRH 2.47/10

Ellern, 1968, 46

A mixture ignites when moistened with water.

Hydrogen sulfide MRH 3.01/30

1. Barrs, C. E., *J. R. Inst. Chem.*, 1955, **79**, 43
2. Mellor, 1947, Vol. 10, 129

Solid sodium peroxide causes immediate ignition in contact with gaseous hydrogen sulfide [1]. Barium peroxides and other peroxides behave similarly [2].

Hydroxy compounds MRH values below reference

Castrantas, 1965, 4

MRH Ethanol 2.43/9, ethylene glycol 2.68/14, glycerol 2.93/17, allose 2.93/17, acetic acid 2.80/16

The exothermic oxidation of ethanol, ethylene glycol, glycerol, sugar or acetic acid may lead to fire or explosion.

See Water, below

See also Ethylene glycol: Oxidants

Magnesium

Bentzinger, von R. *et al., Praxis Naturwiss. Chem.*, 1987, **36**, 38

A priming mixture of magnesium powder and barium peroxide to ignite thermite mixture was to be prepared, but as no barium peroxide was available, sodium peroxide was used instead. Some time after preparation, the mixture ignited spontaneously, because sodium peroxide, unlike barium peroxide, is very hygroscopic and forms hot conc. hydrogen peroxide from contact with atmospheric moisture.

See Carbon dioxide, etc., above

Metal halides

Wiley, J. B. *et al., Mater. Res. Bull.*, 1993, **28**(9), 893

Metathesis reaction to prepare crystalline transition and B metal oxides from halides and sodium peroxide is initiated by a hot wire and can be highly exothermic and explosive in some instances.

See METATHESIS

Metals

MRH Aluminium 4.56/19, iron 1.55/32, magnesium 4.945/24, sodium 2.55/37, tin 1.38/44

Bunzel, E. G. *et al., Z. Anorg. Chem.*, 1947, **254**, 20

At 240°C mixtures of finely divided metals (aluminium, iron, tungsten) with the peroxide ignite under high friction, and molybdenum powder reacts explosively.

Metals, Carbon dioxide, Water

Mellor, 1941, Vol. 2, 490; 1961, Vol. 2, Suppl. 2.1, 633; 1946, Vol. 5, 217

Intimate mixtures of sodium peroxide with aluminium, magnesium or tin powders ignite on exposure to moist air and become incandescent on heating in air or on moistening with water. Exposure of such mixtures to carbon dioxide causes an explosion. (Interaction of the peroxide and carbon dioxide is highly exothermic.) Sodium is oxidised vigorously at 500°C.

Non-metal halides

1. Mellor, 1947, Vol. 10, 897; 1961, Vol. 2, Suppl. 2.1, 634
2. Comanducci, E., *Chem. Ztg.*, 1911, **15**, 706

Violent interactions occur with diselenium dichloride or disulfur dichloride, the latter emitting light and heat [1]. The very exothermic reaction with phosphorus trichloride may accelerate to explosion [2].

Non-metals MRH Carbon 3.05/7, phosphorus 2.30/14, sulfur 3.35/29

1. von Schwartz, 1918, 328
2. Mellor, 1941, Vol. 2, 490
3. Anon., *ABCM Quart. Safety Summ.*, 1948, **19**, 13

Intimate mixtures with carbon or phosphorus may ignite or explode [1]. Other readily oxidisable materials (probably antimony, arsenic, boron, sulfur, selenium) also form explosive mixtures [2]. Use of finely powdered carbon, rather than the granular carbon specified for a reagent, mixed with sodium peroxide caused an explosion [3].

Organic liquids, Water MRH Aniline 2.76/7, benzene 2.76/7, diethyl ether 2.55/8, glycerol 2.72/15

von Schwartz, 1918, 328

Simultaneous contact of sodium peroxide with water and aniline, or benzene, diethyl ether or glycerol, causes ignition: (equivalent to contact with conc. hydrogen peroxide).

Organic material, Water

Bentzinger, von R. *et al., Praxis Naturwiss. Chem.*, 1987, 36, 40

In a combustion demonstration, 50 g of sodium peroxide and half its volume of sago flour are cautiously mixed with a feather. Addition of a few drops of hot water immediately ignites the mixture, which burns vigorously. (The scale of the experiment, using 0.64 mol of sodium peroxide, seems excessive.)

Organic materials

Rüst, 1948, 337

A 'medicinal' mixture of the peroxide (30%) with liquid paraffin (18%), dried soap (42%) and almond oil (10%) ignited explosively during preparation.

Other reactants

Yoshida, 1980, 87—88

MRH values calculated for 30 combinations with oxidisable materials are given.

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

Silver chloride, MRH 0.21/78

Sodium dioxide

See Sodium dioxide: Sodium peroxide

Water

1. *Haz. Chem. Data*, 1975, 269
2. Friend, J. N. *et al., Nature*, 1934, **134**, 778
3. Cheeseman, G. H. *et al., Nature*, 1934, **134**, 971

Reaction with water is vigorous, and with large amounts of peroxide it may be explosive. Contact of the peroxide with combustibles and traces of water may cause ignition [1]. Violent explosions on two occasions during attempted preparation of oxygen were attributed to traces of sodium in the peroxide. The former would liberate hydrogen and ignite the detonable mixture [2,3].

Wood MRH Cellulose 1.97/99+

Dupré, A., *J. Soc. Chem. Ind.*, 1897, **16**, 492

Friction of the peroxide between wooden surfaces caused ignition of the latter.

See other METAL PEROXIDES, OXIDANTS

4798. Sodium thiosulfate

[7772-98-7] $\mathbf{Na_2O_3S_2}$

$Na^+ \quad Na^+ \quad O{=}S(O^-)(S^-){=}O$

HCS 1980, 863

Widmann, G. *et al., Thermochim. Acta*, 1988, **134**, 451—455
Energy of decomposition (320—520°C) was determined by DSC as 2.42 kJ/g, peaking at 427°C.

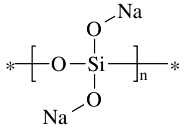
Metal nitrates MRH values show % of nitrate
See Potassium nitrate: Reducants MRH 2.22/50
Sodium nitrate: Sodium thiosulfate MRH 2.38/46

Other reactants
Yoshida, 1980, 230
MRH values calculated for 9 combinations with various materials are given.

Sodium nitrite MRH 2.26/47
Stevens, H. P., *J. Proc. R. Inst. Chem.*, 1946, 285
A mixture of these oxidising and reducing salts will explode violently after most of the water of crystallisation has been driven off by heating.
See other METAL OXONON-METALLATES, REDOX REACTIONS, REDUCANTS

4799. Sodium metasilicate

[6834-92-0] $\mathbf{(Na_2O_3Si)_n}$



Fluorine
See Fluorine: Metal salts
See other METAL OXONON-METALLATES

4800. Sodium sulfate

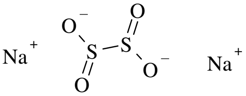
[7681-38-1] $\mathbf{Na_2O_4S}$

$Na^+ \quad Na^+ \quad O{=}S(O^-)(O^-){=}O$

Aluminium
See Aluminium: Sodium sulfate
See other METAL OXONON-METALLATES

4801. Sodium dithionite ('Sodium hydrosulfite') (Sodium dithionate)

[7775-14-6] **$Na_2O_4S_2$**



1. *MCA Case History No. 882*
2. Tyler, B. J. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 45—59, Oxford, Pergamon, 1987
3. Henderson, D. K. *et al., J. Haz. Mat.*, 1988, **19**, 155—159
4. www.chemsafety. gov/circ. US Chem. Safety & Haz. Investigation Board, CSB 1999-4338; 2000-5050

A batch decomposed violently during drying in a graining bowl. No explanation was offered but contamination with water and/or an oxidant seems likely. Thermal decomposition of pure material occurs violently at 190°C [1]. Another batch decomposition, apparently caused by water and leading to a fatality, initiated when an industrial dryer stopped turning, is reported with scant detail [4]. Spontaneous fires or decompositions in industrial use, probably initiated by water, seem common [4]. The sensitivity to water is an expression of the hydration energy of the anhydrous (and impure) salt of commerce. Large quantities of water may be used for fire-fighting. The dihydrate is insensitive to water but contains the water to initiate hydrolytic decomposition, and pressure generation, on heating under containment [Ed.]. Spontaneous ignition of thin layers of sodium dithionite dust was studied experimentally. Ignition temperatures were measured for 5—40 mm layers of mixtures with less than 75% of inert dust. The overall importance of the effect of layer depth on heat transfer parameters at the cold surface was established, and the results were compared with theoretical predictions [2]. Using increasing temperature regimes to determine ignition temperature of dithionite dust layers confirmed the previous value of 190°C, but when decreasing regimes were used the much higher figure of 400°C was found. This was explained on the basis of a 2 stage decomposition characteristic [3].

Aluminium, Water

Kirschner, E., *Chem. Eng. News*, 1995, **73**(18), 6

As part of the process for manufacture of a gold-precipitant, 0.5 tonnes of aluminium powder and 3.5 tonnes of sodium dithionite were in a blender to which benzaldehyde was to be added (other sources also claim presence of potassium carbonate). Either from a leaking seal, or in trying to clear a benzaldehyde feed line, some water was admitted, starting a slow reaction emitting sulphurous fumes. After about eleven hours an attempt was made to blanket with nitrogen (if air had initially been involved, it seems probable the blender had long since purged itself with sulphur dioxide). There was an explosion, followed by fire, killing five workers. In view of the known properties of 'hydros', admission of water might warm localised regions to a temperature where self-sustaining decomposition would ensue in the absence of air. Although a reducing agent in wide use, where aluminium is concerned sodium dithionite and its decomposition products are most definitely oxidants (as is potassium carbonate). Aluminium oxidation was probably responsible for the main blast.

See Aluminium: Metal oxides, or Oxosalts, or Sulfides
See also Water, below

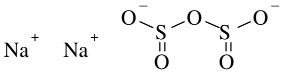
Silver nitrate
See Silver nitrate: Sodium dithionite

Sodium chlorite
See Sodium chlorite: Sodium dithionite

Water
1. Anon., *Chem. Trade J.*, 1939, **104**, 355
2. *MCA Case History No. 2292*
3. Ullmann, 1994, Vol A25, 483
4. Editor's comment

Addition of 10% of water to the solid anhydrous material caused a vigorous exotherm and spontaneous ignition. Bulk material may decompose at 135°C [1]. A loose drum lid allowed ingress of water and smouldering started. As the drum was tipped over for disposal, ignition occurred [2]. Air is usually involved in the exotherm leading to fire after water contamination. The dihydrate may be pyrophoric when finely divided. In the absence of air, exothermic decomposition can occur from 90°C after prolonged heating [3]. Sensitivity to water is an expression of the hydration energy of the anhydrous, and impure, salt of commerce. Large quantities of water will absorb this and can be used for firefighting. The dihydrate is insensitive to water, but contains the water for hydrolytic decomposition, thus the greater thermal sensitivity [4].
See other METAL OXONON-METALLATES, REDUCANTS

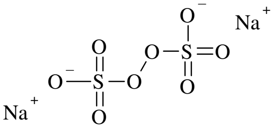
4802. Sodium disulfite ('Sodium metabisulfite')
[7681-57-4] **$Na_2O_5S_2$**



Potassium iodate
See Potassium iodate: Sodium disulfite, Water

Sodium nitrite
See Sodium nitrite: Sodium disulfite
See other METAL OXONON-METALLATES, REDUCANTS

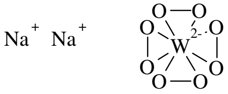
4803. Sodium peroxodisulfate
[7775-27-1] **$Na_2O_8S_2$**



T_{ait24} was determined as 148°C by adiabatic Dewar tests, with an apparent energy of activation of 75 kJ/mol.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

2,2′-Azobis(2-amidiniopropane) chloride
See 2,2′-Azobis(amidiniopropane) peroxodisulfate
See other OXIDANTS, PEROXOACID SALTS

4804. Sodium tetraperoxotungstate
[12501-01-8] **Na_2O_8W**



Mellor, 1943, Vol. 11, 835
It explodes feebly on warming.
See other PEROXOACID SALTS

4805. Sodium sulfide
[1313-82-2, 27610-45-3] (anhydr., hydrate, resp.) **Na_2S**

$Na^+ \ Na^+ \quad S^{2-}$

FPA H115, 1982; *HCS 1980*, 860

1. Anon., *ABCM. Quart. Safety Summ.*, 1942, **13**, 5
2. Dunn, B. W., *Bur. Explos. Accid. Bull., Amer. Rail Assoc.*, 1917, **25**, 36

Fused sodium sulfide in small lumps is liable to spontaneous heating from aerobic oxidation, temperatures of up to 120°C being observed after exposure to moisture and air. Packing in hermetically closed containers is essential [1]. Previously, similar material packed in wooden barrels had ignited in transit [2].
See also SULFUR BLACK

Ammonium persulfate
See Ammonium peroxodisulfate: Sodium sulfide

Carbon MRH 0.041/tr.
Creevey, J., *Chem. Age*, 1941, **44**, 257
Mixtures of sodium sulfide and finely divided carbon exhibit an exotherm on exposure to air. As indicated by the low MRH value, this is probably not a direct interaction, but arises from co-promotion of aerobic oxidation of the individual components.

Diazonium salts
See DIAZONIUM SULFIDES

N,N-Dichloromethylamine
See *N,N*-Dichloromethylamine: Calcium hypochlorite, etc.

Glass

L.B., Personal experience, 1964

An old soda glass bottle of the hygroscopic nonahydrate had become severely etched and corroded internally by the contents, which had leaked through the perforated wall of the bottle. It is probable that the old material had become oxidised by air to a strongly alkaline mixture (below), corrosive to the soft glass.

$2Na_2S + O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$

See other CORROSION INCIDENTS, GLASS INCIDENTS

Hydrogen peroxide

See Hydrogen peroxide: Sulfides

Metal halides

See Tungsten hexachloride: Sodium sulfide

Other reactants

Yoshida, 1980, 392

MRH values calculated for 18 combinations, largely with oxidants, are given.

Sodium carbonate, Water

See SMELT: Water

See other METAL SULFIDES

4806. Sodium disulfide

[22868-13-9] **Na_2S_2**

$Na^+ \quad Na^+ \quad S^- {-} S^-$

Diazonium salts

See DIAZONIUM SULFIDES

See other METAL SULFIDES

4807. Sodium polysulfide

[1344-08-7] **Na_2S_x**

$Na^+ \; S^- {-} S {-} S^- \; Na^+$

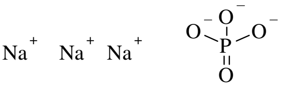
Diazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES

See other METAL SULFIDES

4808. Sodium orthophosphate

[7601-54-9] **Na_3O_4P**



Sugars

See SUGARS

4809. Sodium phosphide

[12058-85-4] **Na_3P**

$Na^+ \quad Na^+ \quad Na^+ \qquad P^{3-}$

Water

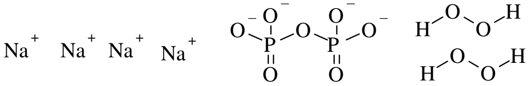
Mellor, 1940, Vol. 8, 834

Sodium phosphide (or potassium phosphide) is decomposed by moist air or water, evolving phosphine, which often ignites.

See other METAL NON-METALLIDES

4810. Sodium pyrophosphate hydrogen peroxidate

[15039-07-3] **$Na_4O_7P_2.2H_2O_2$**



See entry CRYSTALLINE HYDROGEN PEROXIDATES

4811. Niobium

[7440-03-1] **Nb**

Nb

Halogens, or Interhalogens

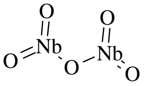
Mellor, 1939, Vol. 9, 849; 1956, Vol. 2, Suppl. 1, 165

Niobium ignites in cold fluorine, and in chlorine at 205°C, and incandesces in contact with bromine trifluoride.

See other METALS

4812. Niobium(V) oxide

[1313-96-8] **Nb_2O_5**



Lithium

See Lithium: Metal oxides

See other METAL OXIDES

4813. Neodymium
[7440-00-8] **Nd**

Nd

Phosphorus
See Phosphorus: Metals
See other METALS

4814. Nickel
[7440-02-0] **Ni**

Ni

RSC Lab. Hazards Data Sheet No. 60, 1987 (Ni and compounds)

1. Sasse, W. H. F., *Org. Synth.*, 1966, **46**, 5
2. Whaley, T. P., *Inorg. Synth.*, 1957, **5**, 197
3. Brown, C. A. *et al., J. Org. Chem.*, 1973, **38**, 2226
4. Savel'eva, O. N., *Chem. Abs.*, 1982, **96**, 165547
5. Anon., *Jahresber.*, 1987, 65

Raney nickel catalysts must not be degassed by heating under vacuum, as large amounts of heat and hydrogen may be evolved suddenly and dangerous explosions may be caused [1]. Nickel powder prepared by several alternative methods may be pyrophoric if particles are fine enough [2]. A non-pyrophoric highly active colloidal hydrogenation catalyst (P-2 nickel) is produced by reduction of nickel acetate in ethanol by sodium tetrahydroborate [3]. Catalytic Raney nickel electrodes are rendered non-pyrophoric by aqueous metal nitrate treatment [4]. After storage for some time, a drum containing Raney nickel catalyst under water was opened for inspection. As the lid was being removed, there was an explosion which blew it up into the air. This is attributed to desorption of hydrogen into the air-space to form an explosive mixture, and ignition of the latter by traces of dry (and pyrophoric) catalyst in the top of the drum which sparked in contact with the ingress of air as the lid was opened. It was suggested that such stored drums should be shaken to wet any catalyst at the top of the drum before opening. Displacing any air with carbon dioxide before sealing would seem also to be advisable [5].

Aluminium
See Aluminium—nickel alloys

Aluminium chloride, Ethylene
See Ethylene: Aluminium chloride

1,4-Dioxane MRH 1.46/99+
See 1,4-Dioxane: Nickel

Hydrogen
1. Adkins, H. *et al., J. Amer. Chem. Soc.*, 1948, **70**, 695
2. Adkins, H. *et al., Org. Synth.*, 1955, Coll. Vol. 3, 176

3. Chadwell, A. J. *et al., J. Phys. Chem.*, 1956, **60**, 1340

During hydrogenation of an unspecified substrate (possibly 4-nitrotoluene) at high pressure with the highly active W6 type of Raney nickel catalyst at 150°C, a sudden exotherm caused the initial pressure to double rapidly to 680 bar [1]. This does not happen at 100°C or below. Care is necessary with selection of reaction conditions for highly active catalysts [2]. Hydrogen-laden Raney nickel catalyst when heated strongly under vacuum undergoes explosive release of the sorbed hydrogen [3].

Hydrogen, Oxygen

Lee, W. B., *Ind. Eng. Chem., Prod. Res. Dev.*, 1967, **6**(1), 59—64

Raney nickel powder entrained in cryogenic hydrogen gas causes ignition on contact with liquid or cryogenic gaseous oxygen.

See other CATALYTIC IMPURITY INCIDENTS

Magnesium silicate

Blake, E. J., private comm., 1974

The pyrophoricity of nickel-on-sepiolite catalysts after use in petroleum processing operations may be caused by the presence of finely divided nickel and/or carbon.

See other PYROPHORIC CATALYSTS

Methanol

1. *MCA Case History No. 1225*
2. Anon., *Jahresber.*, 1983, 77—78
3. Anon., *Sichere Chemiearbeit*, 1990, **42**, 45

Ignition occurred when methanol was poured through the open manhole of a 230 l reactor containing Raney nickel catalyst. Although the reactor had been purged thoroughly with nitrogen before opening, it was later shown that air was entrained during pouring operations, and this would cause nickel particles round the manhole opening to glow. A closed charging system was recommended [1]. A slurry of Raney nickel catalyst in methanol was to be added to a nitrogen-filled reactor containing a methanol solution. A valve connecting the reactor to a closed circuit acid-scrubber was opened to equalise the pressure, but the scrubber was at a rather lower pressure and reduced the pressure in the total system below ambient. When the charging port was opened, air was drawn in carrying residual catalyst particles into the vessel and ignition occurred. Remedial measures are outlined [2]. An identical ignition injuring two workers is reported subsequently [3].

Non-metals

Mellor, 1942, Vol. 15, 148, 151

On heating, mixtures of powdered nickel with sulfur or selenium react incandescently.

See Sulfur compounds, below

Organic solvents

Hotta, K. *et al., Chem. Abs.*, 1969, **70**, 81308

Raney nickel catalyst evaporated with small amounts of methanol, ethanol, isopropanol, pentanol, acetone, benzene, cyclohexane or *p*-dioxane and then heated towards 200°C eventually explodes

See 1,4-Dioxane: Nickel

Other reactants

Yoshida, 1980, 270

MRH values calculated for 14 combinations, largely with oxidants, are given.

Oxidants

	MRH values show % of oxidant
See Ammonium nitrate: Metals	MRH 2.59/58
Bromine pentafluoride: acids, etc.	MRH 3.64/55
Chlorine: Metals	MRH 2.34/55
Nitryl fluoride: Metals	
Peroxyformic acid: Metals	MRH 5.69/99+
Potassium perchlorate: Metal powders	MRH 2.64/37

Sulfur compounds

Kornfeld E. C., *J. Org. Chem.*, 1951, **16**, 137

Raney nickel catalyst, containing appreciable amounts of the sulfide (after use to desulfurise thioamides) is rather pyrophoric.

See other HYDROGENATION CATALYSTS, METALS, PYROPHORIC METALS

4815. Nickel(II) oxide

[1313-99-1] **NiO**

$$\mathrm{Ni{=}O}$$

Anilinium perchlorate

See Anilinium perchlorate: Metal oxides

Fluorine

See Fluorine: Metal oxides

Hydrogen peroxide

See Hydrogen peroxide: Metals, etc.

Hydrogen sulfide

See Hydrogen sulfide: Metal oxides

See other METAL OXIDES

4816. Nickel(IV) oxide

[12035-36-8] **NiO_2**

$$\mathrm{O{=}Ni{=}O}$$

Fluorine

See Fluorine: Metal oxides

See other METAL OXIDES

4817. Nickel(III) oxide

[1314-06-3] **Ni_2O_3**

$Ni^{3+}\quad Ni^{3+}\ O^{2-}\ O^{2-}\ O^{2-}$

Hydrogen peroxide

See Hydrogen peroxide: Metals, etc.

Nitroalkanes

See NITROALKANES: Metal oxides
See other METAL OXIDES

4818. Lead(II) oxide

[1317-36-8] **OPb**

$Pb{=}O$

Aluminium carbide

Mellor, 1946, Vol. 5, 872
The carbide is oxidised with incandescence on warming with lead oxide.
See Metal acetylides, below

Chlorinated rubber

See CHLORINATED RUBBER: Metal oxides

Chlorine, Ethylene

See Chlorine: Hydrocarbons (references 1,4)

Dichloromethylsilane

See Dichloromethylsilane: Oxidants

Fluorine, Glycerol

See Fluorine: Miscellaneous materials (reference 1)

Fluoroelastomers

Simpson, M. B. H., *Kautsch. Gummi, Kunstst.*, 1980, **33**, 83—85
Dispersions of lead oxide in fluoroelastomers underwent severe exothermic decomposition when heated above the normal mixing temperature of below 200°C, forming elemental lead.

Glycerol, Perchloric acid

See Perchloric acid: Glycerol, etc.

Hydrogen trisulfide

See Hydrogen trisulfide: Metal oxides

Linseed oil

Stolyarov, A. A., *Chem. Abs.*, 1935, **29**, 3860_3

Spontaneous ignition occurring during the early stages of mixing and grinding the components was traced to individual grades of lead oxide and the presence of undispersed lumps in the mixture.

Metal acetylides

Mellor, 1945, Vol. 5, 849

Interaction at 200°C with rubidium acetylide is explosive, and with lithium acetylide, incandescent.

Metals

Mellor, 1946, Vol. 5, 217; 1941, Vol. 7, 116, 656—658

Mixtures of the oxide with aluminium powder give a violent or explosive ‘thermite’ reaction on heating. Finely divided sodium ignites on admixture with the oxide, and a mixture of the latter with zirconium explodes on heating. Titanium is also oxidised violently on warming.

Non-metals

1. Mellor, 1941, Vol. 7, 657
2. Goodfield, J. A. C. *et al., Fuel*, 1982, **61**, 843—847

A mixture with boron incandesces on heating, and with silicon the reaction is vigorous. If aluminium is present the mixture explodes on heating (but the same is true if silicon is absent) [1]. The pyrotechnic reaction of boron and lead oxide mixtures has been studied by DSC [2].

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

Seleninyl chloride

See Seleninyl chloride: Metal oxides

See other METAL OXIDES, OXIDANTS

4819. Palladium(II) oxide

[1314-08-5] **OPd**

$$\mathrm{Pd{=}O}$$

Hydrogen

Sidgwick, 1950, 1558

It is a strong oxidant and glows in contact with hydrogen at ambient temperature.

See other METAL OXIDES, OXIDANTS

4820. Thorium oxide sulfide

[12218-77-8] **OSTh**

$$\mathrm{S{=}Th{=}O}$$

Mellor, 1941, Vol. 7, 240

It ignites in contact with air.

See other PYROPHORIC MATERIALS

See related METAL OXIDES, METAL SULFIDES

4821. Zirconium oxide sulfide

[12164-95-3] **OSZr**

$\mathrm{S{=}Zr{=}O}$

Sorbe, 1968, 160

It ignites in air.

See other PYROPHORIC MATERIALS

See related METAL OXIDES, METAL SULFIDES

4822. Silicon oxide

[10097-28-6] **OSi**

$\mathrm{Si{=}O}$

Zintl, E. et al., *Z. Anorg. Chem.*, 1940, **245**, 1

The freshly prepared material ignites in air.

See other NON-METAL OXIDES, PYROPHORIC MATERIALS

4823. Tin(II) oxide

[21651-19-4] **OSn**

$\mathrm{Sn{=}O}$

Bailar, 1973, Vol. 2, 64

On heating at 300°C in air, oxidation proceeds incandescently.

Non-metal oxides

Mellor, 1941, Vol. 7, 388

The oxide ignites in nitrous oxide at 400°C, and incandesces when heated in sulfur dioxide.

See other METAL OXIDES

4824. Zinc oxide

[1314-13-2] **OZn**

$\mathrm{Zn{=}O}$

NSC 267, 1978; *HCS 1980*, 968

Aluminium, Hexachloroethane

See Hexachloroethane: Metals

Chlorinated rubber

See CHLORINATED RUBBER: Metal oxides

Linseed oil

Anon., *Chem. Trade J.*, 1933, **92**, 278

Slow addition of zinc white (a voluminous oxide containing much air) to cover the surface of linseed oil varnish caused generation of heat and ignition. Lithopone, a denser (air-free) grade of oxide did not cause heating.

Magnesium

See Magnesium: Metal oxides

See other METAL OXIDES

4825. Oxygen (Gas)

[7782-44-7] **O_2**

$$O=O$$

NSC 472, 1977; *FPA H12*, 1973; *HCS 1980*, 708

1. Anon., *Sichere Chemiearbeit*, 1994, **46**(8), 94

Even a slight increase in the oxygen content of air above its usual 21 vol.% will greatly increase the rate of oxidation or combustion of many substances, including the human anatomy. An autoclave for hot oxygen treatment (900°C, 406 bar) was located in a bunker. To purge it with argon for cooling it was necessary to enter the bunker and open a valve. This discharged hot oxygen into a pipe and ignited a plastic seal, thence the metal of the pipe, then combustible contents of the bunker burnt explosively in the escaped oxygen. The operator was killed immediately [1]. Low concentrations of oxygen in other gases may be concentrated as liquid when working at low temperatures.

See Oxygen (Liquid)

See OXYGEN ENRICHMENT

Acetaldehyde

See Acetaldehyde (references 2,4)

Acetone

Anon., private comm., 1988

To ‘ensure proper ignition’ during oxygen-flask analysis, a technician put a single drop of acetone onto the filter paper enclosing the sample, before igniting the tail and insertion into the oxygen-filled flask. An explosion followed which shattered the flask, fortunately enclosed in a mesh screen which retained the fragments. It was calculated that 0.07 ml of acetone would have formed an explosive vapour—air mixture in the flask above the lower explosive limit, so considerably less acetone would have given an explosive mixture in the oxygen atmosphere.

See Barium acetate: Copper(II) oxide, etc.

Acetone, Acetylene

Anon., *CISHC Chem. Safety Summ.*, 1976, **47**, 33—34

A combination of faulty equipment and careless working led to an extremely violent explosion during oxy-acetylene cutting work. The oxygen cylinder was nearly empty

and the regulator had a cracked diaphragm. The acetylene cylinder was lying on its side and was feeding a mixture of liquid acetone and acetylene gas to the burner head. When the oxygen ran out, the excess pressure from the acetylene line forced the acetone—acetylene mixture back up the oxygen line and into the cylinder via the cracked diaphragm. The explosion destroyed the whole plant.
See Acetylene: Oxygen

Acetylene
Skobelar, V. F., *Chem. Abs.*, 1981, **94**, 120243
A safe method for demonstrating explosive combustion of acetylene—oxygen mixtures in bubbles is described.

Alkali metals
1. Mellor, 1941, Vol. 2, 469
2. Sidgwick, 1950, 65

Reactivity towards air or oxygen increases from lithium to caesium, and the intensity depends on state of subdivision and on presence or absence of moisture. Lithium normally ignites in air above its m.p., while potassium may ignite after exposure to atmosphere, unless it is unusually dry. Rubidium and caesium ignite immediately on exposure [1]. It is reported that sodium and potassium may be distilled unchanged under perfectly dried oxygen [2].

Alkaline earth metals
Mellor, 1941, Vol. 3, 637—638
Finely divided calcium may ignite in air, and the massive metal ignites on heating in air, and burns vigorously at 300°C in oxygen. Strontium and barium behave similarly.

Aluminium—titanium alloys
See Aluminium—titanium alloys: Oxidants

Ammonia
Rüst, 1948, 332—333
Accidental connection of an oxygen cylinder to top-up an ammonia-containing refrigeration system led to explosive destruction of the compressor.

Ammonia, Platinum
1. Nealy, D., and Williams, E. J. *et al., School Sci. Rev.*, 1935, **16**(63), 410
2. Long, G. C., *Spectrum* (Pretoria), 1980, **18**, 30

In school demonstrations of the oxidation of ammonia to nitric acid over platinum catalysts, substitution of oxygen for air causes fairly vigorous explosions to occur [1]. Practical details are given [2].

1,4-Benzenediol, 1-Propanol
1. Burgiel, J. C. *et al., J. Chem. Phys.*, 1965, **43**, 4291
2. Anon., *Univ. Safety Assoc. Safety News*, 1978, (9), 11—12; Peacock, C. J., private comm., 1978

The solid inclusion (clathrate) complex of oxygen with hydroquinone had been prepared twice previously by a published method which involved saturating a solution of hydroquinone in propanol in an autoclave at 70°C with oxygen at 20—150 bar,

followed by slow cooling under oxygen pressure (and most probably without stirring to allow large crystals of the inclusion complex to form) [1]. In a third attempt, (to produce smaller crystals free of the 'quinhydrone complex' impurity) a solution was prepared and saturated with oxygen at 80 bar, then heated to 90°C (when the partial pressure of oxygen would increase to around 100 bar), then allowed to cool with agitation. After 20 min the bursting disk failed at 450 bar and an explosion damaged the autoclave and premises [2]. Without agitation, the rate of oxidation of the solvent and hydroquinone would be controlled by diffusion of oxygen through the (small) gas liquid interface. With agitation, the rate of oxidation would be expected to increase greatly, and lead to runaway oxidation with very fast increase in temperature and pressure and explosive combustion when the autoignition temperature (371°C for propanol in air at 1 bar, less in oxygen) were attained.
See Hydrocarbons (reference 3), below

Benzoic acid

1. Corbett, R. A., private comm., 1976
2. Wilson, L. Y. et al., *J. Chem. Educ.*, 1985, **62**(10), 902

Benzoic acid is burned in oxygen as a primary thermochemical standard to calibrate oxygen bomb calorimeters used in the IP12/ASTM D240 standard tests for determination of calorific value of liquid hydrocarbon fuels. If the benzoic acid is powdered (rather than pelleted as IP12 recommends), very rapid combustion occurs and the flame front may burn through the non-metallic (Teflon) seals on valve seats and the bomb may be destroyed [1]. Ignition of a pelleted sample in a bomb with a faulty closure valve led to sudden venting of combustion gases which blew off the insulating cover and thermometer. Safety precautions are listed for bomb calorimetry work [2].

Biological material, Ether

Napier, D. H., private comm., 1972

Biological material in a polythene bag filled with oxygen and being prepared for analytical combustion exploded. Diethyl ether used to anaesthetise the experimental animal from which the sample was derived may have still been present, and ignition from static charge on the plastics bag may have been involved.
See related STATIC INITIATION INCIDENTS

Boron tribromide
See Arsine—boron tribromide

Bromine, Chlorotrifluoroethylene
See Bromine: Chlorotrifluoroethylene, Oxygen

Calcium phosphide
See Calcium phosphide: Oxygen

Carbon disulfide

Dudkin, V. A., *Chem. Abs.*, 1982, **97**, 203762

The lower limit for spontaneous ignition of mixtures with oxygen has been studied.

Carbon disulfide, Mercury, Anthracene

Anon., *ABCM Quart. Safety Summ.*, 1953, **25**, 2

Shortly after mercury was accidentally introduced into a system containing a solution of anthracene in carbon disulfide under an atmosphere of oxygen, an explosion occurred. Presence of mercury may have catalysed rapid oxidation of carbon disulfide.
See other CATALYTIC IMPURITY INCIDENTS

Carbon monoxide, Hydrogen
Schierwater, F.-W., *Sichere Chemiearb.*, 1985, **37**(9), 101—102
Synthesis gas ($CO + H_2$) at 40 bar containing a low level of hydrogen sulfide was to be freed of the latter impurity by adding the theoretical quantity of oxygen and passing the mixture over a catalyst. Introduction of oxygen (from a supply at 60 bar) via a simple T-piece (instead of through the recommended small bore coaxial injection nozzle to ensure thorough mixing with the gas stream) caused development of an intense inverse flame in the locally very high oxygen concentration which burned through the reactor side wall opposite the oxygen inlet and ejected a metre-long flame-jet.

Copper, Hydrogen sulfide
See Hydrogen sulfide: Copper, Oxygen

Cyclohexane-1,2-dione bis(phenylhydrazone)
1. Schulze, M. *et al., Z. Chem.*, 1979, **19**, 210—211
2. Adam, W. A. *et al., Tetrahedron*, 1985, **41**, 2045—2056

Autoxidation of the hydrazone (O_2/C_6H_6/UV) gives the explosive isomeric 1,2-dihydroperoxy-1,2-bis(benzeneazo)cyclohexane [1], and the same is true for COT derivatives [2].
See 1,2-Dihydroperoxy-1,2-bis(benzeneazo)cyclohexane
See α-PHENYLAZO HYDROPEROXIDES

Cyclooctatetraene
Adam, W. A. *et al., Tetrahedron Lett.*, 1982, **23**, 3156
In a procedure to oxygenate photochemically COT to the 1,4-endoperoxide, highly explosive undefined polymeric peroxides are formed as by-products.
See other POLYPEROXIDES

Diborane
See Diborane: Oxygen

Diboron tetrafluoride
See Diboron tetrafluoride: Oxygen

Dimethoxymethane
See Dimethoxymethane: Oxygen

Dimethyl sulfide
Harkness, A. C. *et al., Atmos. Environ.*, 1967, **1**, 491—497
Interaction is explosive at 210°C or above, and the mechanism has been studied.

Dimethylketene
See Poly(peroxyisobutyrolactone)

Ethers

Davies, 1961, 79

Many ethers, either of open chain (diethyl or diisopropyl ether) or cyclic type (tetrahydrofuran, dioxane), are readily autoxidised on exposure to air or oxygen in presence of light. The hydroperoxides formed are less volatile than the parent ether and may be concentrated to a dangerous extent if distillation of peroxidised material is attempted.

See AUTOXIDATION, PEROXIDES IN SOLVENTS

Fibrous materials

1. Anon., *Loss Prev. Bull.*, 1978, (020), 49
2. Anon., *Sichere Chemiearbeit*, 1991, **43**(10), 112
3. Anon., *Loss Prev. Bull.*, 1978, (023), 141—143

Most fibrous fabrics will sorb oxygen when exposed to concentrations greater than the normal 21% in air, and this is retained for a long time after excess oxygen is no longer present, greatly increasing the possibility of ignition. Hose leakage led to oxygen enrichment inside a vessel in which welding was taking place. A welder lit a cigarette but did not appreciate the significance of its rapid combustion and the unusually long lighter flame. Sparks from welding later ignited clothing, leading to fatal burns [1]. Accidental connection of a pneumatic grinder to an oxygen line instead of a compressed air line led to ignition of the apprentices' clothing when the grinder was started. Another grinding incident occurred in the open air near the vent of a liquid oxygen tank, not only clothing but the worker's hair and beard ignited [2]. Accidental connection of a breathing set to an oxygen cylinder rather than to a medical air cylinder caused ignition of the facepiece [3].

See OXYGEN ENRICHMENT

Fluorine, Hydrogen

See Fluorine: Hydrogen, Oxygen

Fluorocarbons (including perfluorocarboms)

See FLUOROCARBONS: Oxygen

Fuel gases

NFPA 51, Quincy (Ma), Natl. Fire Prot. Assocn., 1984

The US fire code covers installation and use of gaseous oxygen—fuel gas systems for welding and cutting, for the thermodynamically unstable fuels acetylene, MAPP (methylacetylene—allene—propene—propane mixtures), and the stable hydrocarbons propane or butane.

Fuels

1. Ivanov, B. A. *et al., Chem. Abs.*, 1975, **82**, 75130
2. Rasbash, D. J., *Fire Saf. J.*, 1986, **11**, 113—125
3. Plewinsky, B. *et al., Prax. Sicherheitstech.*, 1997, **4**, 95

Possible reasons for explosions of 40 l steel cylinders containing oxygen at or below 150 bar are discussed. Presence of a substantial (0.1—0.2 mm) layer of mineral oil, or more likely, ingress of a combustible gas from a higher-pressure source, are possibilities [1]. The major factors affecting the occurrence and progress of explosions in mixtures of air with flammable gases, vapours, mists and dusts are discussed. These include flammability limits, burning velocity in laminar and turbulent conditions, possible onset of detonation, pressure piling, etc. [2]. A review, with references, of detonation in systems with gaseous oxidants and condensed fuels, with particular relevance to the design of oxidation reactors, has been published [3] .

See Hydrocarbons, below

See Oil films, below

Glycerol

Smith, B. S., *Chem. Abs.*, 1978, **89**, 47649

Glycerol is oxidised at an appreciable rate by high-pressure oxygen in the presence of copper alloys to give glyceric acid, oxalic acid and formic acid, which lead to severe corrosion of the alloy. Malfunction of aircraft oxygen gauges operating at 125 bar was attributed to blockage of the brass Bourdon tubes by copper salts of the acids produced by long-term oxidation of residual traces of glycerol—water solutions used for gauge testing.

See other CORROSION INCIDENTS

Halocarbons

1. Fawcett, H. H., *Chem. Eng. News*, 1957, **35**(43), 60
2. Weber, U., *Chim. Ind.* (Paris), 1963, **90**, 178
3. Bashford. L. A. *et al., J. Chem. Soc.*, 1938, 1064
4. Haszeldine, R. N. *et al., J. Chem. Soc.*, 1959, 1085—1086

1,1,1-Trichloroethane exploded after heating under oxygen at 54 bar and 100°C for 3 h [1]. Trichloroethylene, remaining in a pipe after cleaning operations, exploded under 27 bar pressure of oxygen at ambient temperature. It was later found possible to explode stoicheiometric mixtures [2]. Chlorotrifluoroethylene and bromotrifluoroethylene each react explosively with oxygen at ambient temperature [3], but controlled oxidation of the former produces an explosive cyclic peroxide, 4.5-dichloro-3,3,4,5,6,6-hexafluoro-1,2-dioxane [4].

See Oxygen (Liquid): Halocarbons
Iodomethane: Oxygen

See Tetrafluoroethylene

Hydrocarbons

1. Davies, 1961, 11
2. Staudinger, H., *Z. Elektrochem.*, 1925,**31**, 549
3. Unpublished information, 1968
4. Burgess, G. K., *Ind. Eng. Chem.*, 1930, **22**, 473
5. Francis, C. K., *Ind. Eng. Chem.*, 1930, **22**, 896
6. Hunn, E. B., *Ind. Eng. Chem.*, 1930, **22**, 804
7. Dunn., B. W., *Bur. Expl. Accid. Bull., Amer. Rail Assoc.*, 1924, **32**(1), 1—2
8. Anon., *CISHC Chem. Safety Summ.*, 1977, **48**, 8
9. Anon., *Loss Prev. Bull.*, 1978, (020), 49
10. Davies, R., *Loss Prev.*, 1979, **12**, 103—110
11. Kletz, T. A., *Loss Prev.*, 1979, **12**, 96—102
12. Herrmann, G. *et al.*, Ger. Offen. DE 3 514 924, 1986

Interaction of hydrocarbons with gaseous oxygen may be slow or fast, depending on conditions and substrate, but peroxidic products are always involved, and the rate of formation is highest at a C—H link adjacent to an aromatic ring or a double bond [1]. Predictable conditions for explosion are those relevant to the internal combustion engine (Otto or Diesel types). Unpredicted conditions include the following cases. During studies on autoxidation of 1,1-diphenylethylene with oxygen at high pressure and low temperature an explosion occurred [2]. Partial oxidation of a gasoline fraction in an autoclave under oxygen, initially at 22 bar and 100°C, ran wild and exploded; several smaller reactions had proceeded uneventfully [3]. Previously oxidation reactions of gasoline at 20 bar/105°C had exploded [4], and a severe explosion occurred while admitting oxygen, virtually at 1 bar pressure, to an autoclave containing a glass bottle of gasoline [5]. Precautions were detailed later [6].

An attempt to decarbonise a gasoline motor cycle engine by inserting a lighted match through the spark plug hole into the cylinder, and then blowing in oxygen, caused a violent explosion to occur [7]. Comment seems superfluous. Lack of a duplicate oxygen monitor on a plant in which oxygen and hydrocarbon were mixed led to a violent explosion during the hour-long daily monitor-checking procedure [8]. Use of oxygen instead of compressed air to start a diesel engine, or to clear a blocked petrol pipe, led to violent explosions [9]. In an overview of hazards of industrial air-oxidation processes, they are all identified as inherently hazardous, and the majority extremely so. Particular hazards are detailed, and major incidents involving liquid phase oxidation of cyclohexane or cumene, and vapour phase oxidation of ethylene to the oxide are listed, together with the causes [10]. Further examples of the causes of fires in the last 3 processes, and in the liquid phase oxidation of *p*-xylene to terephthalic acid are given [11]. A technique for liquid-phase oxidation of hydrocarbons in a vertical column containing a bottom water layer and no gas-phase above the hydrocarbon layer is claimed to be free of the danger of detonation [12].
See Buten-3-yne: Oxygen
See Fuel gases, above
See Fuels, above
See Oil films, below
See Tetracarbonylnickel: Oxygen,
See also Hydrogen, above
See also BITUMEN

Hydrocarbons, Promoters
Barisov, A. A. *et al., Chem. Abs.*, 1984, **101**, 93812
Among other compounds, methyl nitrate, nitromethane, ethyl nitrate and tetrafluorohydrazine function as promoters of spontaneous ignition of mixtures of methane or propane with oxygen and argon.

Hydrogen
1. Bailey, D. J. C., *Chem. & Ind.*, 1954, 492
2. Cook, M. A. *et al., Chem. Eng. News*, 1956, **34**, 4436
3. Weissveiler, A., *Z. Elektrochem.*, 1936, **42**, 499
4. Carty, P., *School Sci. Rev.*, 1978, **59**(208), 517—518
5. Loubeyre, P. *et al., Nature*, 1995, 378, 44

6. Editor's comments

When oxygen was passed through a drying tower containing activated alumina previously used to dry hydrogen, explosions occurred. Nitrogen purging between changing gases would prevent this [1]. During preparation of stoicheiometric mixtures in a steel mixing tank (at 17—82 bar, with or without 15% argon), several spontaneous explosions occurred during valve manipulation at 30 min after mixing, but not 10 min after mixing. A possible catalytic effect of the surface of the steel tank was eliminated by coating it thinly with silcone grease [2]. There is a narrow range of concentrations in which the mixture is supersensitive to initiation [3]. A simple and safe method of demonstrating the explosive combustion of stoicheiometric hydrogen—oxygen mixtures with spark ignition in a polythene bottle is described [4]. It is claimed that, at ultra-high pressure, hydrogen and oxygen mixtures become non-explosive [5]. Since an extremely small test apparatus is involved and no consideration given to critical diameter or other surface effects, this is open to doubt [6].

Hydrogen sulfide

See Hydrogen sulfide: Oxygen

Lithiated dialkylnitrosamines

Mochizuki, M., *Tetrahedron Lett.*, 1980, **21**, 1766

Oxygenation of lithiated dialkylnitrosamines in THF at —78°C is fast and gives good yields of the *N*-alkyl-*N*-(1-hydroperoxyalkyl)nitrosamines. If oxygenation is too prolonged, poor yields and explosive by-products result.

Mercury, Tetracarbonylnickel

See Tetracarbonylnickel: Mercury, etc.

Metal hydrides

1. Mellor, 1941, Vol. 2, 483
2. Mackay, 1966, 30, 67

Sodium hydride ignites in oxygen at 230°C, and finely divided uranium hydride ignites on contact. Lithium hydride, sodium hydride and potassium hydride react slowly in dry air, while rubidium and caesium hydrides ignite. Reaction is accelerated in moist air, and even finely divided lithium hydride ignites then [1]. Finely divided magnesium hydride, prepared by pyrolysis, ignites immediately in air [2].

See also COMPLEX HYDRIDES

Metals

1. Heinicke, G., *Technik*, 1969, **24**, 313—319
2. Hirano, T. *et al., J. Loss Prev.*, 1993, **6**(3), 151
3. Newton, B. *et al., ASTM Special Technical Publication STP1454*, 2003, 268

General data on fire hazards present in industrial oxygen-producing plants are given with details of experimental study of factors involved in combustion of various metals and alloys used in such plant. Safety in selection of materials is discussed [1]. A study of combustion of structural metals (Fe, Al) in oxygen is given [2]. Fires do occur within oxygen systems, generally starting at valves where friction can abrade protective oxides [3].

See Oxygen (Liquid): Metals

See also Aluminium: Oxygen

Methoxy-1,3,5,7-cyclooctatetraene
See Methoxy-1,3,5,7-cyclooctatetraene: Oxygen

4-Methoxytoluene
Imamura, J. *et al.*, Brit. Pat. 1 546 397, 1979
Liquid phase oxidation of 4-methoxytoluene to anisaldehyde at 60 bar/115°C in acetic acid containing heavy metal salts is violent, and must be controlled by the rate of addition of oxygen gas.

Non-metal hydrides
1. Mellor, 1946, Vol. 5, 36
2. Sidgwick, 1950, 344, 553
3. Mellor, 1940, Vol. 6, 220—225

The reported ignition of diborane and tetraborane(10) in contact with air or oxygen is due to the presence of traces of silicon hydrides [1]. The lower members of the latter class ignite or explode in air or oxygen, especially at reduced pressure [2]. Phosphine is also sensitive [3].
See Aluminium tetrahydroborate: Alkenes, Oxygen
Decaborane(14)
Pentaborane(11)
Phosphine: Oxygen

Oil films
Werley, B. M., *ASTM Spec. Tech. Publ.*, 1983, (812), 108—125
The hazards arising from presence of oil films in oxygen-handling systems are reviewed, with consideration of cleanliness specifications, film flammability, film migration and hazard mechanisms.
See Hydrocarbons, above

Organic analytical samples
1. Pack, D. E., *Chem. Eng. News*, 1966, **44**(2), 4
2. Devereaux, H. D., *Chem. Eng. News*, 1966, **44**(6), 4
3. Heysel, R. M. *et al., Chem. Eng. News*, 1966, **44**(10), 4
4. MacDonald, A. M. G., *Chem. Eng. News*, 1966, **44**(19), 7
5. Jenkin, J. B., *Chem. & Ind.*, 1974, 585
6. Guthrie, R. D. *et al., Chem. Brit.*, 1979, **15**, 614; *J. Chem. Educ.*, 1980, **57**(3), 226

Hazards involved in the use of the oxygen flask combustion technique are discussed and illustrated with several examples [1]. Some explosions occurred after completion of combustion, when the oxygen concentration in the flask is still some 75% [2]. Shielding of the flask [3], minimally with wire gauze [4] seems advisable. Explosion during a blank combustion (of a folded filter paper) was attributed possibly to thermal strains. Similar occurrences had been noted previously [5]. Fitting a simple pressure relief (Bunsen) valve to the flask improves safety aspects, and the oxygen flask method is also to be preferred (for qualitative work) to the more hazardous sodium fusion method [6].
See Sodium: Halocarbons, or: Organic analytical samples

Organic materials

Burnett, R. J. *et al., J. Chem. Educ.*, 1985, **62**(5), A157, A159

Facilities and procedures necessary to encourage safety in laboratory work involving oxidation of organic materials with pressurised oxygen are reviewed.

Ozone, Rubber

See Ozone: Oxygen, Rubber

Pentaborane(9)

See Pentaborane(9): Oxygen

Perfluorocarbons

See FLUOROCARBONS: Oxygen

Phosphine

See Phosphine: Oxygen

Phosphorus tribromide

Bailar, 1973, Vol. 2, 426

Oxidation of the bromide with gaseous oxygen is not easily controlled and becomes explosive.

Phosphorus(III) oxide

See Tetraphosphorus hexaoxide: Oxygen

Plastic cylinder caps

Anon., *Loss Prev. Bull.*, 1978, (020), 49

The plastic caps (or tape) which cover the outlets on refilled oxygen cylinders will burn readily in oxygen and must be completely removed and no bits trapped in the fittings attached to the cylinder outlet.

See Organic materials, above

Plastic tubes

1. Wolf, G. L. *et al., Anaesthesiology*, 1987, **67**, 236—239
2. Davies, P., Personal communication, 1993

Following fires in which endotracheal tubes became ignited by surgical lasers or electrocautery in atmospheres enriched by oxygen and/or nitrous oxide, the flammability of PVC, silicone rubber and red rubber tubes in enriched atmospheres was studied [1]. Ozonised oxygen was reacted with hydrogen at low pressure to generate hydroxyl radicals. Pressure in the apparatus was maintained by a vacuum pump protected from ozone by a tube of heated silver foil. On two occasions there was an explosion in the plastic vent pipe from the vacuum pump. The vent gas should have been outside explosive limits and the exact cause is not clear; the editor suspects peroxide formation.

Polymers

1. *MCA Case History No. 395*
2. *MCA Case History No. 1111*
3. *491M*, 1975, 294

A foam rubber sample, being tested for oxidation resistance under oxygen at 34 bar at 90°C exploded with extreme violence after 4 days [1]. Use of a Neoprene-lined hose in a high-pressure oxygen manifold caused failure and ignition of the burst hose. Possible ignition sources include adiabatic compressive heating, and friction from vibration of metal reinforcing fibres in the high velocity stream of escaping oxygen [2]. Polytetrafluoroethylene (Teflon) ignited at 705°C in oxygen at 0.34 bar pressure when used as wire insulation, while polyolefine insulation ignited at 593°C under the same conditions [3].

Polytetrafluoroethylene, Stainless steel

Anon., *Petroleum Rev.*, 1979, 48

In two test methods (IP40, IP38) for the oxidative stability of hydrocarbons, samples are heated in a valve-sealed stainless bomb under an oxygen atmosphere. On several occasions minor explosions occurred when valves with Teflon sealing discs (rather than the older metal needle closures) were operated during oxygen purging or venting operations. (This was associated with presence of metal particles and traces of grease being embedded in the Teflon discs). Only stainless needle valves, and a controlled rate of pressure release, are recommended for these tests.

See PERFLUOROCARBONS

Propylene oxide

See Propylene oxide: Oxygen

Rhenium

Mellor, 1942, Vol. 12, 471

The metal ignites in oxygen at 300°C.

Rubberised fabric

Anon., *Loss Prev. Bull.*, 1978, (020), 52

Accidental connection of a cylinder of oxygen instead of medical air to an air breathing set led to ignition of the face-piece.

sec-Alcohols

1. Davies, 1961, 80
2. Redemann, E. G., *J. Amer. Chem. Soc.*, 1942, **64**, 3049

Secondary alcohols are readily autoxidised in contact with oxygen or air, forming ketones and hydrogen peroxide [1]. A partly full bottle of 2-propanol exposed to sunlight for a long period became 0.36 M in peroxide and potentially explosive [2].

See 2-Butanol

See Hydrogen peroxide: Acetone, or: Alcohols

See 2-Propanol: 2-Butanone

Tetrafluoroethylene

1. Pajaczkowski, A., *Chem. & Ind.*, 1964, 659
2. Ger. Pat. 773 900, 1971

Accidental admixture of oxygen gas with unstabilised liquid tetrafluoroethylene produced a polymeric peroxide which was powerfully explosive, and sensitive to heat, impact or friction [1]. Removal of oxygen by treatment with pyrophoric copper to prevent explosion of tetrafluoroethylene has been claimed [2].

See other POLYPEROXIDES

Tetramethyldisiloxane

1. Anon., *Jahresber.*, 1983, 71—72
2. Plewinsky, B. *et al., Thermochim. Acta*, 1985, **94**, 33—42
3. Plewinsky, B., *Chem. Abs.*, 1990, **113**, 234231

A 4.9 g sample of the liquid siloxane in a glass dish was put into a bomb calorimeter (on an open bench) containing 5 ml of sodium hydroxide solution to absorb combustion gases. The electric igniter system consisted of a metal wire in contact with a cotton-wool wick which dipped into the siloxane sample. The bomb was sealed, pressured up to 39—44 bar with oxygen, and the igniter was fired. A violent explosion blew the lid off the bomb (rated at 190 bar working, 250 bar test), and examination of the deformed bomb indicated that a maximum detonation pressure of around 900 bar had been attained.

Detailed examination of the reaction showed a 2 stage mechanism. Hydrolysis of the volatile partially methylated siloxane by the alkaline solution liberated hydrogen which formed an explosive mixture with oxygen. When the igniter was fired, the hydrogen—oxygen explosion atomised the remaining liquid siloxane leading to a very violent secondary explosion. The wick also played a decisive separate role, as the siloxane-soaked cotton also underwent extremely rapid detonative decomposition on ignition. The rate of pressure rise was measured as 10 kbar/s, with a maximum pressure calculated for a 4.9 g sample of 800 bar. Hexamethyldisiloxane (which cannot produce hydrogen by hydrolysis) burned smoothly under the same conditions. It is recommended that no more than 0.5 g samples should be used, with oxygen pressure limited to 20 bar and protective enclosure of the bomb equipment [1]. A more detailed investigation of the combustion of tetramethyldisiloxane in oxygen showed that, even in the absence of hydrogen, combustion was still extremely violent, the rate of pressure increase being inversely proportional to the pressure of oxygen, as expected for a homogeneous gas-phase combustion reaction. The unusually high rate of pressure rise (265 kbar/s, to max 113 bar for 10 bar oxygen pressure) is indicative of detonation. Under heterogeneous conditions, liquid tetramethyldisiloxane gave a maximum rate of pressure rise of 90 kbar/s to max 160 kbar with 30 bar oxygen pressure, with an abrupt change to the higher values between 15 and 20 bar oxygen pressure [2]. Further study showed that detonation-like transmission of combustion across the surface of either a soaked wick, or bulk liquid, could take place with a gas-phase composition below the lower flammability limit [3]. Pentamethyldisiloxane showed generally similar behaviour (maximum rate 38 kbar/s to max 205 bar for 30 bar oxygen pressure), with an abrupt increase between 25 and 30 bar pressure of oxygen [2].

See SILANES; OXYGEN BOMB CALORIMETRY

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Titanium

Anon., *ABCM Quart. Safety Summ.*, 1962, **33**, 24

Passage of oxygen through a titanium feed pipe into a titanium autoclave caused a titanium—oxygen fire and explosion at 44 bar. When the surface oxide film is

damaged, titanium can ignite at 24 bar under static conditions and at 3.4 bar under dynamic conditions, with oxygen at ambient temperature.
See Aluminium—titanium alloys: Oxidants

Titanium trichloride, Vapours of low ignition temperatures
Huneker, K. H., *Chem. Abs.*, 1977, **87**, 15458
The Dräger oxygen-measuring tube contains titanium trichloride as the indicating substance, and a possible hazard in using these tubes to measure oxygen contents above 25 vol% in gas mixtures has been noted. The temperature in the tube can reach 120°C during oxidation of titanium trichloride to titanium dichloride oxide, so the test should not be used if compounds with ignition points below 135°C (e.g. carbon disulfide) are present.

Trirhenium nonachloride
1. Edwards, P. G. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 2467, 2472
2. Edwards, P. G., *Lab. Haz. Bull.*, 1984(4), 3, item 212

During preparation of perrhenyl chloride by combustion of rhenium nonachloride in an oxygen stream [1], a violent explosion, possibly involving chlorine oxides, occurred on heating the chloride to 250°C. A safe procedure involving heating the chloride to 250°C under nitrogen, and then introducing oxygen, is proposed [2].
See other NON-METALS, OXIDANTS

4826. Oxygen (Liquid)
[7782-44-7] **O_2**

$O{=}O$

HCS 1980, 709

NFPA 50, Quincy (Ma), Natl. Fire Prot. Assoc., 1985
The US National Fire Code covers all aspects of equipment, installation and safe operational practices necessary for bulk oxygen storage at consumer sites.

Author's comments
Although the entries below refer to the specific hazards observed with a few organic or oxidisable materials, it is probable that most organic materials, inorganic reducing agents, and many unoxidised inorganic materials may be highly hazardous with liquid oxygen under approprate conditions of contact and initiation. Liquid oxygen also implies a region of oxygen enriched atmosphere near the vent of a storage vessel, or during transfer; this has its own hazards.

Acetone
Blau, K., private comm., 1965
Accidental addition of liquid oxygen to vacuum jars containing acetone residues from trap-cooling use caused a violent explosion. Liquid nitrogen is less hazardous as a trap coolant, but only under controlled conditions.
See Nitrogen (Liquid)

Acetylene, Oil

Basyrov, Z. B. *et al., Chem. Abs.*, 1960, **54**, 12587a

The detonation capacity of mixtures of acetylene and liquid oxygen is increased by the presence of organic material (oils) in the oxygen. Hazards of accumulation of oil in air-liquefaction and -fractionation plants are emphasised.

See Hydrocarbons, below

Ammonia, Ammonium nitrate, Diphenyl carbonate

Buzard, J. *et al., J. Amer. Chem. Soc.*, 1952, **74**, 2925—2926

During the synthesis of ^{15}N-labelled urea by interaction of labelled ammonium nitrate, liquid ammonia and diphenyl carbonate in presence of copper powder, a series of explosions of the refrigerated sealed tubes was encountered. This was almost certainly caused by condensation of traces of oxygen in the tubes cooled to —196°C during condensation of ammonia before sealing the tubes. Cooling to —80°C would have been adequate and have avoided the hazard.

See Nitrogen (Liquid)

Asphalt

1. Weber, U., *Chim. et Ind.* (Paris), 1963, **90**, 178
2. English, W. D. *et al., Chem. Eng. News*, 1992, **70**(10), 18
3. Gayle, B., *Rev. Tech. Feu*, 1979, **20**(189), 62

Mechanical impact on a road surface on to which liquid oxygen had leaked caused a violent explosion [1]. Anecdotal evidence that there have been several like incidents is given [2]. Mixtures of asphalt and liquid oxygen were shown to be impact-sensitive on the small scale, but on the larger scale a detonator was necessary to initiate mild explosion of liquid oxygen on a layer of asphalt [3]. Oil, rubber or other impurities may have been present on the road surface in the first incident.

See OXYGEN ENRICHMENT

See other CRYOGENIC LIQUIDS

Carbon

1. Kirshenbaum, 1965, 4
2. Stettbacher, A., *Spreng-u. Schiess-Stoffe*, 71, Zurich, Racher, 1948
3. Angot, A., *Ann. Mines [13]*, 1934, **5**, 46—51
4. Hempseed, J. W. *et al., Plant/Oper. Progr.*, 1991, **10**(3), 184

Mixtures of carbon and liquid oxygen have been used as blasting explosives for some time [1,2], Mixtures with carbon black appear unusually sensitive to impact, and a blasting cartridge exploded when dropped [3]. Purification of helium containing only 1.4% oxygen and 0.7% nitrogen by passing through a carbon absorber at —195°C led to an explosion of 20kg TNT equivalent. It was found that a liquid phase of 85% oxygen content was capable of condensing onto the carbon at the entry.

Carbon, Iron(II) oxide

Leleu, *Cahiers*, 1975, (78), 121

Carbon containing 3.5% of the oxide explodes on contact with liquid oxygen.

See other CATALYTIC IMPURITY INCIDENTS

Halocarbons

Anon., *Chem. Eng. News*, 1965, **43**(24), 41

Mixtures of liquid oxygen with dichloromethane, 1,1,1-trichloroethane, trichloroethylene and 'chlorinated dye penetrants 1 and 2' exploded violently when initiated with a blasting cap. Carbon tetrachloride exploded only mildly, and a partly fluorinated chloroalkane not at all. Trichloroethylene has been used for degreasing metallic parts before use with liquid oxygen, but is not safe.

See Oxygen (Gas): Halocarbons

Hexafluoropropene, Oxygen difluoride

See Oxygen difluoride: Hexafluoropropene, etc.

Hydrocarbons

1. Mellor, 1941, 1, 379
2. Kirshenbaum, 1956, 17, 22
3. *MCA Case History No. 865*
4. Wright, G. T., *Chem. Eng. Progr.*, 1961, **57**(4), 45—48
5. Rotzler, R. W., *et al., Chem. Eng. Progr.*, 1960, **56**(6), 68—73
6. Matthews, L. G., *Chem. Eng. Progr.*, 1961, **57**(4), 48—49
7. Karwat., E., *Chem. Eng. Progr.*, 1958, **54**(10), 96—101
8. Streng, A. G. *et al., J. Chem. Eng. Data*, 1959, **4**, 127—131
9. Pelman, M., *AD Rep. 768744/5GA*, Springfield (Va.), USNTIS, 1973
10. Gustov, V. F. *et al., Chem. Abs.*, 1984, **100**, 12006

Mixtures of hydrocarbons with liquid oxygen are highly dangerous explosives, not always requiring external initiation. The earliest example must be that of Claudé, who accidentally knocked a lighted candle into a bucket of liquid oxygen in 1903 and suffered from the violent explosion ensuing [1]. Mixtures with liquid methane or benzene are specifically described as explosive [2]. Traces of oil in a liquid oxygen transfer pump caused the explosion described in the Case History [3]. Mixtures with petroleum and absorbent charcoal have been used experimentally as blasting explosives [1]. Addition of a little aluminium powder to liquid methane—oxygen mixtures increases the explosive power [2]. An explosion in a liquid oxygen evaporator was attributed to the presence of acetylene, arising from unusual plant conditions and higher than usual hydrocarbon concentrations in the atmospheric air taken in for liquefaction [4]. Two similar explosions in main condensers were attributed to presence of acetylene [5] or unspecified hydrocarbons [6]. Suitable precautions are detailed in all cases. Experimental work appeared to implicate ozone as a major contributory factor [7].

The explosive properties of liquid methane—oxygen mixtures were determined [8]. During investigation of an explosion in a portable air liquefaction—separation plant, hydrocarbon oil was found in a silica filtration bed [9]. The mechanism of slow heterogeneous accumulation of hydrocarbons dissolved in trace amounts in liquid oxygen on the liquid evaporator surfaces is discussed. It was concluded that months of continuous evaporation would be required to attain explosion-hazardous levels in real evaporators [10].

Hydrogen (Liquid)

See Hydrogen (Liquid): Oxygen

Liquefied gases

1. Kirshenbaum, 1956, 17, 30, 34
2. Lester, D. H., *Rept. NASA-CR-148711*, Richmond (Va), USNTIS, 1976

Mixtures with liquid carbon monoxide, cyanogen (solidified), and methane are highly explosive [1]. Autoignition in liquid oxygen—hydrogen propellant systems has been reviewed [2].

Lithium hydride

Kirshenbaum, 1956, 44

Mixtures of lithium hydride powder and liquid oxygen are detonable explosives of greater power than TNT.

Metals

1. Anon., *Chem. Eng. News*, 1957, **35**(24), 90
2. Anon., *Chem. Eng. News*, 1957, **35**(31), 10
3. Austin, C. M. *et al., J. Chem. Educ.*, 1959, **36**, 54, 308
4. *MCA Case History No. 824*
5. Kirshenbaum, 1956, 4, 16
6. *MCA Case History No. 988*
7. Strauss, W. A., *Amer. Inst. Aeronaut. Astronaut. J.*, 1968, **6**, 1753
8. Rozovskii, A. S. *et al., Chem. Abs.*, 1979, **91**, 23447
9. Lewis, D. J., *Haz. Cargo. Bull.*, 1983, **4**(11), 28—29
10. Bodner, G. M., J. *Chem. Educ.*, 1985, **62**(12), 1106

A demonstration of combustion of aluminium powder in oxygen exploded violently, probably owing to presence of unevaporated liquid at ignition [1]. Stoicheiometric mixtures of the two are explosives much more powerful than TNT [2]. Further details and comments were given later [3]. An aluminium filter in a high-capacity liquid oxygen transfer line exploded violently, possibly owing to friction or impact ignition of an aluminium component in contact with an abrasive particle, which would penetrate the protective oxide layer [4]. Powdered magnesium, titanium or zirconium mixed with liquid oxygen are detonable [5]. A nitrogen-pressurised liquid oxygen dispenser made of titanium alloy failed during nitrogen pressurising. The vessel failed because of reaction of the titanium alloy with liquid oxygen. Titanium is more reactive towards oxygen than either stainless steel or aluminium, and should therefore not be used for oxygen service, either gas or liquid [6]. Mixtures of liquid oxygen with 48—64 wt% of fine aluminium powder are detonable, and the parameters were investigated [7]. Detonation of mixtures with powdered aluminium, iron, titanium and chromium—nickel alloy powders was studied [8]. A new liquid oxygen road tanker constructed of aluminium ruptured violently during manoeuvring operations after a delivery, when the contents had been pressured up with gaseous oxygen (evaporated from the liquid) to expel the liquid. The rupture was traced to erosion and thinning of the tank wall adjacent to an internal baffle joint, where aluminium particles, oil and a halocarbon degreasing solvent were trapped in a cavity in the weld. These had reacted with the pressurising oxygen atmosphere, raising the wall

temperature in the vapour space to that where direct reaction of the aluminium container with gaseous oxygen was possible. Some 70 kg of metal was missing in all [9]. Accounts of many further accidents in lecture demonstrations of rapid combustion of aluminium powder—liquid oxygen mixtures have been published [10].
See Aluminum: Oxidants
See also Magnesium: Oxidants

Organic materials
1. Hauser, R. L. *et al., Adv. Cryog. Eng.*, 1962, **8**, 242—250
2. Clippinger, D. E. *et al., Aircraft. Eng.*, 1959, **32**(365), 204—205

Many common polymers, polymeric additives and lubricants oxidise so rapidly after impact in liquid oxygen that they are hazardous. Of those tested, only acrylonitrile—butadiene, poly(cyanoethylsiloxane), poly(dimethylsiloxane) and polystyrene exploded after impact of 6.8—95 J intensity (5—70 ft.lbf). All plasticisers (except dibutyl sebacate) and antioxidants examined were very reactive. A theoretical treatment of rates of energy absorption and transfer is included [1]. Previously, many resins and lubricants had been examined similarly, and 35 were found acceptable in liquid oxygen systems [2].

Preparative hazard
Anon., *Sichere Chemiearbeit*, 1994, **46**(8), 94
During regeneration of an adsorber in the cold box of an air separation plant, regeneration gas exited via the adsorber drain pipe. This still contained some liquid oxygen. Very low regeneration-gas flows permitted desorption of acetylene and other hydrocarbons at above normal (ppm) concentrations, these condensed or crystallised into the liquid oxygen and the mixture finally detonated, causing limited damage. It is recommended that regeneration gas should never be vented via the drain pipe.
See Hydrocarbons, below

1,3,5-Trioxane
Kirshenbaum, 1956, 31
Mixtures with liquid oxygen are highly explosive.

Wood (+ charcoal)
1. Weber, U., *Chim. et Ind.* (Paris), 1963, **90**, 178
2. Lang, A., *Chem. Eng. Progr.*, 1962, **58**(2), 71

Several major accidents during handling of tonnage amounts of liquid oxygen are described [1]. One involved a violent explosion caused by leakage of liquid oxygen on to metal-encased timber (which previously had been charred) and spark ignition from welding in the oxygen-enriched atmosphere of an air-separation plant [2].
See other CRYOGENIC LIQUIDS, NON-METALS, OXIDANTS

4827. Osmium(IV) oxide
[12036-02-1] **O_2Os**

$O{=}Os{=}O$

Preparative hazard

Sidgwick, 1950, 1493

The amorphous form, prepared by dehydration at low temperature, is a pyrophoric powder.

See Sodium chlorate: Osmium

See other METAL OXIDES, PYROPHORIC MATERIALS

4828. Lead(IV) oxide (Lead dioxide)

[1309-60-0] **O_2Pb**

$$O{=}Pb{=}O$$

HCS 1980, 590

Carbon black, Chlorinated paraffin, Manganese(IV) oxide

1. Rasmussen, B., *Unwanted chemical reactions; Appendix B*, Risø I-279, Risø National Laboratory, Roskilde (DK), 1987; *J. Haz. Mat.*, 1988, **19**, 279—288
2. Author's comments to Dr Rasmussen, 1988

During the established manufacture of an accelerator mixture for a joint-filling composition, carbon black, lead(IV) oxide and manganese(IV) oxide were dispersed in a mixture of viscous chlorinated paraffins in presence of a silicone surfactant by agitation in a 1200 l reactor. The mixture was subsequently milled in a continuously fed shear disk bead mill to reduce the particle size and increase the degree of dispersion to a predetermined value. The bulk temperature of the material was increased to 55°C by the milling operation, and it was returned to the reactor for storage before re-milling, as the particle size was too coarse. After 2 days, exothermic decomposition set in with evolution of hydrogen chloride and probably chlorine also, and the mixture in the reactor eventually ignited. The reactor was eventually quenched with water and was found to contain a solid resiidue resembling clinker.

Some variations from the normal routine had occurred in the course of preparing this batch, including:- addition of a major portion of the chlorinated paraffin to the reactor which still contained 100—150 kg of a previous batch of accelerator, followed by standing for 16 days over a winter holiday break; use of 20% more manganese dioxide than usual; the mixture had not dispersed properly during the normal single milling pass, so had to be stored.

Subsequent investigation of the incident was undertaken both by DSC and by both 5 kg and 1 kg simulations of the incident in electrically heated glass or metal reaction vessels. DSC showed that the stabilised chlorinated paraffin began to decompose exothermally only above 300°C, with $\Delta H = 1.25$ kJ/g, while the reaction mixture showed an initial exotherm at 91°C, with the main exotherms above 200°C, and $\Delta H = 3.64$ kJ/g. The 5 kg process simulation experiment showed that non-acidic gas began to be evolved at about 150°C, and no hydrogen chloride was evolved until after the reaction mixture had been heated for several hours at temperatures up to about 200°C (during which period the inhibitor had probably been consumed). Further heating to 220°C initiated a thermal runaway reaction, with temperatures exceeding 300°C and violent evolution of white fumes, which continued (without external heating) for over an hour. The residue was a grey clinker, samples of which showed a relatively much lower lead content and higher manganese content than the original mixture. The addition of ferric chloride to the chlorinated paraffin caused considerable reduction of the thermal stability of the latter.

It was concluded that the reaction mixture was thermally unstable if subjected to thermal initiation, and that temperatures of over 300°C were capable of attainment, when direct reaction between the metal oxides amd the chlorinated paraffins or their degradation products were possible. The origin of the heat energy necessary to increase the temperature of the milled batch from 55 to 91°C (the DSC-identified exotherm teperature) could not be identified [1].

However, a reasonable and coherent explanation seems possible if the following assumptions are made.

1. During the 16-day contact of the first 250 kg portion of chlorinated paraffin with the 150 kg residue of previously processed accelerator, the 1% inhibitor content of the former became depleted or exhausted by adsorption and/or reaction, reducing the thermal stability of the liquid phase.

2. During the 2 day storage (apparently without agitation) of the milled reaction mixture, initially at 55°C, the oxidants (mainly lead dioxide) began to react with the carbon black (effectively a very finely divided organic fuel), the 12.5 kg of which could release up to 373 MJ of heat if oxidised fully to carbon dioxide. The heat release may well have not been uniform throughout the batch, probably being concentrated in the bottom of the unstirred batch, where the not fully dispersed lead dioxide (d. = 9.4) would settle out. This heat release may have been sufficient to increase the temperature, at least locally, to 91°C, when the total exotherm would then have been increased.

3. Once the thermal runaway had become established, the high temperature could allow a ‘smelting reaction’ (reduction of lead oxides by carbon to metallic lead) to occur, and the low m.p. and high density (327°C, 10.6, respectively) would cause the molten lead to concentrate at the base of the reactor, decreasing the lead content and raising the manganese content of the bulk of the clinker residue, as was observed [2].

See other AGITATION INCIDENTS, INDUCTION PERIOD INCIDENTS, REDOX REACTIONS

Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Hydrogen sulfides MRH Hydrogen sulfide 0.56/82

Mellor, 1941, Vol. 7, 689; 1947, Vol. 10, 129, 159

Contact of hydrogen sulfide with dry or moist lead dioxide causes attainment of red heat and ignition. Contact of hydrogen trisulfide with the dioxide causes violent decomposition and ignition.

Metal acetylides or carbides

Mellor, 1946, Vol. 5, 850, 872

Interaction with aluminium carbide is incandescent, and with caesium acetylide at 350°C is explosive. Other related compounds may be expected to be oxidised violently if unmoderated.

Metal sulfides

Mellor, 1941, Vol. 3, 745

Calcium sulfide, strontium sulfide or barium sulfide react vigorously with lead dioxide on heating.

Metals MRH Magnesium 3.22/17

1. Mellor, 1963, Vol. 2, Suppl. 2.2, 1571
2. Mellor, 1940, Vol. 4, 272
3. Mellor, 1946, Vol. 5, 217
4. Mellor, 1941, Vol. 7, 658, 691
5. Collvin, P., *Chem. Abs.*, 1982, **96**, 87999

Warm potassium reacts explosively with lead dioxide, and sodium probably behaves similarly [1]. Magnesium reacts violently [2], and powdered aluminium probably does also, as it reacts violently with the monoxide [3]. Mixtures of powdered molybdenum or tungsten with the dioxide incandesce on heating [4]. The combination with zirconium is rated highest on a scale for sensitivity to deflagration, friction, ignition and static electrical initiation [5].

See other STATIC INITIATION INCIDENTS

Nitroalkanes

See NITROALKANES: Metal oxides

Nitrogen compounds MRH Hydroxylamine 1.92/36

1. Mellor, 1941, Vol. 7, 637
2. Mellor, 1940, Vol. 8, 291

Hydroxylamine ignites in contact with lead dioxide [1], while phenylhydrazine immediately reacts vigorously [2].

Non-metal halides MRH Phosphorus trichloride 0.67/31

1. Mellor, 1941, Vol. 7, 690
2. Mellor, 1947, Vol. 10, 676, 909

Warm phosphorus trichloride reacts with incandescence [1] and seleninyl chloride vigorously. Sulfonyl dichloride may react explosively [2].

Non-metals

1. Mellor, 1946, Vol. 5, 17
2. Mellor, 1941, Vol. 7, 689—690
3. Gibson, N., *Runaway Reactions*, 1981, Paper 3/R, 6

Boron or yellow phosphorus explode violently on grinding with lead dioxide, while red phosphorus ignites [1]. Mixtures with sulfur ignite on grinding or addition of sulfuric acid [2]. An initiating mixture of silicon and lead dioxide (2:1) attains a temperature around 1100°C after ignition by a small flame [3].

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

Potassium

See Potassium: Metal oxides

Sulfur dioxide

Mellor, 1941, Vol. 7, 689
Interaction is incandescent.
See other METAL OXIDES, OXIDANTS

4829. Palladium(IV) oxide

[12036-04-3] **O_2Pd**

$O{=}Pd{=}O$

Bailar, 1973, Vol. 3, 1279

The hydrated oxide is a strong oxidant, and slowly evolves oxygen at ambient temperature.

See other METAL OXIDES, OXIDANTS
See related PLATINUM COMPOUNDS

4830. Platinum(IV) oxide

[1314-15-4] **O_2Pt**

$O{=}Pt{=}O$

Acetic acid, Hydrogen

Adams, R. *et al., Org. Synth.*, 1941, Coll. Vol. 1, 66

Addition of fresh platinum oxide catalyst to a hydrogenation reaction in acetic acid caused immediate explosion. Several similar incidents, usually involving acetic acid as solvent, are known to the author.

See other METAL OXIDES, OXIDANTS, PLATINUM COMPOUNDS

4831. Sulfur dioxide

[7446-09-5] **O_2S**

$O{=}S{=}O$

(*MCA SD-52*, 1953); *HCS 1980*, 876 (cylinder)

Barium peroxide
See Barium peroxide: Non-metal oxides

Boranes
See BORANES: ALUMINIUM CHLORIDE, SULFUR DIOXIDE

Caesium azide
See Caesium azide: Sulfur dioxide

Diethylzinc
See Diethylzinc: Sulfur dioxide

Halogens, or Interhalogens MRH values show % of interhalogen
See Bromine pentafluoride: Acids, etc. MRH 1.72/53

See Chlorine trifluoride: Metals, etc. MRH 2.43/74
See Fluorine: Non-metal oxides MRH 5.10/64

Lithium acetylide—ammonia
See Monolithium acetylide—ammonia: Gases, etc.

Lithium nitrate, MRH 1.00/30
Metal acetylides
Mellor, 1946, Vol. 5, 848—849
Monocaesium acetylide or monopotassium acetylide, and the ammoniate of monolithium acetylide all ignite and incandesce in unheated sulfur dioxide. The dimetal derivatives including sodium acetylide appear to be less reactive, needing heat before ignition occurs.

Metal oxides MRH Iron(II) oxide 1.21/40
1. Mellor, 1941, Vol. 2, 487
2. Mellor, 1942, Vol. 13, 715
3. Mellor, 1941, Vol. 7, 388, 689

Caesium oxide [1], iron(II) oxide [2], tin oxide and lead(IV) oxide [3] all ignite and incandesce on heating in the gas.

Metals MRH Chromium 3.39/52, manganese 2.89/46, sodium 4.56/26
1. Mellor, 1943, Vol. 11, 161
2. Mellor, 1942, Vol. 12, 187
3. Gilbert, H. N., *Chem. Eng. News*, 1948, **26**, 2604
4. Mellor, 1961, Vol. 2, Suppl. 2.1, 468

Finely divided (pyrophoric) chromium incandesces in sulfur dioxide [1], while pyrophoric manganese burns brilliantly on heating in the gas [2]. Molten sodium reacts violently with the dry gas or liquid, while the moist gas reacts as vigorously as water with cold sodium [3].

Other reactants
Yoshida, 1980, 267
MRH values calculated for 12 combinations with various materials are given.

Peat
Byrne, P. J., *Chem. Abs.*, 1976, **104**, 21731
Treatment of peat stockpiles with sulfur dioxide surprisingly accelerated the self-heating process.

Polymeric tubing
MCA Case History No. 1044
Plastics tubing normally capable of withstanding an internal pressure of 7 bar failed below 2 bar when used to convey gaseous sulfur dioxide.

Potassium chlorate MRH 1.80/44
See Potassium chlorate: Sulfur dioxide

Preparative hazard
See Sulfuric acid: Copper

Propene MRH 2.18/30
See Propene: Lithium nitrate, etc.

Silver azide
See Silver azide: Sulfur dioxide

Sodium hydride MRH 3.72/23
See Sodium hydride: Sulfur dioxide
See other NON-METAL OXIDES, REDUCANTS

4832. Selenium dioxide

[7446-08-4] **O_2Se**

$O{=}Se{=}O$

HCS 1980, 814

1,3-Bis(trichloromethyl)benzene
See 1,3-Bis(trichloromethyl)benzene: Oxidants

Phosphorus trichloride
Mellor, 1940, Vol. 8, 1005
A mixture of the cold components attains red-heat.
See other OXIDANTS
See related METAL OXIDES

Preparative hazard
See Selenium: Oxygen, Organic matter

4833. Silicon dioxide (Silica)

[7631-86-9] **O_2Si**

$O{=}Si{=}O$

HCS 1980, 819

Hydrochloric acid
MCA Case History No. 1857
A glass drying trap on a hydrochloric acid storage tank was filled with silica gel instead of the calcium sulfate specified. The glass trap fractured, probably owing to thermal shock from the much higher heat of adsorption of water and hydrogen chloride on silica gel.
See other GLASS INCIDENTS

Metals
See Magnesium: Silicon dioxide
Sodium: Non-metal oxides

Oxygen difluoride
See Oxygen difluoride: Adsorbents

Ozone
See Ozone: Silica gel

Silicone liquid, Unstated salt
See SILICONE LIQUID: Silica, etc.

Steel

These two anciently served as a means of ignition. They still can. Although the sparking of flint and steel is strictly a mechanical phenomenon, any subsequent fires will not be. Other forms of silica still serve as igniters to this day, via the piezoelectric effect.
See GRAVEL

Vinyl acetate
See Vinyl acetate: Desiccants

Xenon hexafluoride
See Xenon hexafluoride: Silicon dioxide
See other NON-METAL OXIDES

4834. Tin(IV) oxide
[18282-10-5] **O_2Sn**

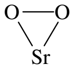
$O{=}Sn{=}O$

Chlorine trifluoride
See Chlorine trifluoride: Metals, etc.

Hydrogen trisulfide
See Hydrogen trisulfide: Metal oxides

Metals
See Aluminium: Metal oxides
Magnesium: Metal oxides
Potassium: Metal oxides
Sodium: Metal oxides
See other METAL OXIDES

4835. Strontium peroxide
[1314-18-7] **O_2Sr**



Organic materials
Haz. Chem. Data, 1975, 272

Mixtures of the peroxide with combustible organic materials very readily ignite on friction or contact with moisture.
See other METAL PEROXIDES

4836. Titanium(IV) oxide (Titanium dioxide)

[13463-67-7] **O_2Ti**

O=Ti=O

HCS 1980, 903

Metals

Mellor, 1941, Vol. 7, 10, 44; 1961, Vol. 2, Suppl. 2.1, 81
Reduction of the oxide by aluminium, calcium, magnesium, potassium, sodium or zinc is accompanied by more or less incandescence (lithium, magnesium and zinc especially).
See other METAL OXIDES

4837. Uranium(IV) oxide

[1344-57-6] **O_2U**

O=U=O

Mellor, 1942, Vol. 12, 42
The finely divided oxide prepared at low temperature is pyrophoric when heated in air, and burns brilliantly.
See other METAL OXIDES, PYROPHORIC MATERIALS

4838. Tungsten(IV) oxide

[12036-22-5] **O_2W**

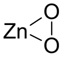
O=W=O

Chlorine

See Chlorine: Tungsten dioxide
See other METAL OXIDES

4839. Zinc peroxide

[1314-22-3] **O_2Zn**



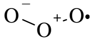
Alone, or Metals

1. Mellor, 1940, Vol. 4, 530
2. Sidgwick, 1950, 270

The hydrated peroxide (of indefinite composition) explodes at 212°C [1], and mixtures with aluminium or zinc powders burn brilliantly [2].
See other METAL PEROXIDES

4840. Ozone (Trioxygen)

[10028-15-6] **O_3**



HCS 1980, 710 (cyl., dissolved gas); *RSC Lab. Hazards Data Sheet No. 66*, 1987

1. Sidgwick, 1950, 860
2. Adley, F. E., *Nucl. Sci. Abs.*, 1962, **17**, 18
3. Streng, A. G., *Explosivstoffe*, 1960, **8**, 225
4. Clough, P. N. *et al., Chem. & Ind.*, 1966, 1971
5. Gatwood, G. T. *et al., J. Chem. Educ.*, 1969, **46**, A103
6. Loomis, J. S. *et al., Nucl. Instr. Methods*, 1962, **15**, 243
7. Brereton, S. J., *Fusion Technol.*, 1988, **15**(2 pt.23), 833
8. *Ozone Reactions with Organic Compounds*, ACS 112, Washington, ACS, 1972
9. Walker, K. G., *Chem. Brit.*, 1987, **23**, 839
10. Ogle, R. A. *et al., Process Safety Progr.*, 1998, **17**(2), 127
11. Koike, K. *et al., J. Chem. Eng. Jap.*, 1999, **32**(3), 295
12. www.umdrij.edu/eohssweb/aiha/accidents/glass

Ozone is strongly endothermic (ΔH_f° (g) +142.2 kJ/mol, 2.96 kJ/g) and the pure solid or liquid materials are highly explosive. Evaporation of a solution of ozone in liquid oxygen causes ozone enrichment and ultimately explosion [1]. Organic liquids and oxidisable materials dropped into liquid ozone will also cause explosion of the ozone [2]. Ozone technology and hazards have been reviewed [3], a safe process to concentrate ozone by selective adsorption on silica gel at low temperatures has been described [4], and safe techniques for laboratory generation and handling of ozone have been detailed [5]. Ozone has become available as a dissolved gas in cylinders. Explosive hazards involved in use of liquid nitrogen as coolant where ozone may be incidentally produced during operation of van der Graaff generators [6] and radiation sources [7], etc. have been discussed. The chemistry of interaction with organic compounds has been extensively reviewed [8]. Methods and equipment for generation of ozone (up to 13%) in oxygen and storage at high pressure and low temperature for extended periods are described [9]. An explosion downstream of an industrial ozoniser is described, a leak in the cooling system let oil enter the ozonised airstream. The surplus airstream was fed to a manganese dioxide catalyst bed for ozone destruction. An explosion in this bed resulted. The oil was too involatile to make an explosion with the ozonised air probable. It was not possible to trigger untoward events by contact of oil and catalyst in the laboratory, though this is the cause ascribed. Changes induced in the oil by prior ozonolysis have been largely neglected (this would certainly have increased the volatility and might also have led to the incorporation of peroxide groups) [10]. Ozone in air at 1 bar is not explosive below 10% concentration. Reduction in pressure shifts explosive limit to higher concentration. Carbon dioxide shows a weak inhibitory effect [11]. Introduction of ozone, presumably with a carrier, into an organic liquid cooled to —85°C, below the usual temperature of ozonolysis, produced a deep blue colour, indicating accumulation, followed by explosion. The colour might serve as a warning indicator [12].

See Silica gel, below

Acetylene

Grignard, 1935, Vol. 3, 166

Passage of ozone (endothermic oxidant) into acetylene (endothermic reducant) leads to a violent explosion when 50 mg/l of ozone is present.

See other REDOX REACTIONS

Alkenes

1. Sidgwick, 1950, 862
2. Davies, 1961, 97
3. Stull, 1977, 21

Interaction of alkenes with ozonised oxygen tends to give several types of products or their polymers, some of which show more pronounced explosive tendencies than others [1]. The cyclic *gem*-diperoxides are more explosive than the true ozonides [2]. It has been calculated that ozonisation of the endothermic *trans*-stilbene (ΔH_f° +135.4 kJ/mol, 0.78 kJ/g) would give, in the event of decomposition of the unstable ozonide, an exothermic release of 1.41 kJ/g which would attain an adiabatic decomposition temperature approaching 750°C with a 27-fold pressure increase in a closed vessel [3].

See CYCLIC PEROXIDES

Alkylmetals

Lee, H. U. *et al., Combust. Flame*, 1975, **24**, 27—34

The spectra of flames from spontaneous interaction of ozone with dimethylzinc and diethylzinc in a flow system have been studied.

Allyl bromide

Ohio State University, www.chemistry.ohio-state.edu/safety

A violent explosion was experienced at 50°C when attempting to distil the products of ozonolysis in dichlormethane. At this temperature the solvent would have evaporated, leaving ozonide.

See Alkenes, below

See OZONIDES

Ammoniacal vapours

1. Bond, 1991, 31
2. Anon., *Fire Prevention*, 1986, (191), 45

Vent air from an animal facility was deodourised by ozone treatment; an extensive fire was started by cutting into the polypropylene ducting carrying the treated air to atmosphere. This was attributed to formation of ammonium nitrate by ammonia oxidation, which mixed with organic dusts also present in the vent-line [1]. A more detailed account of the incident reveals that initial ignition was probably by sawing into metal. Ozone was also found to have degraded the polypropylene pipework, increasing flammability (peroxide formation?) [2].

See Ammonium nitrate

Aromatic compounds

Mellor, 1941, Vol. 1, 911

Benzene, aniline and other aromatic compounds give explosive gelatinous ozonides, among other products, on contact with ozonised oxygen.

Benzene, Oxygen, Rubber

Morrell, S. H., private comm., 1968

During ozonisation of rubber dissolved in benzene, an explosion occurred. This seems unlikely to have been owing to formation of benzene triozonide (which separates as a gelatinous precipitate after prolonged ozonisation), since the solution remained clear. A rubber ozonide may have been involved, but the benzene—oxygen system itself has high potential for hazard.

Bromine

Lewis, B. *et al., J. Amer. Chem. Soc.*, 1931, **53**, 2710

Interaction becomes explosive above 20°C and a minimum critical pressure.

See Hydrogen bromide, below

See also Bromine trioxide

Charcoal, Potassium iodide

Anon., *Lab. Haz. Bull.*, 1983(9), 3, item 660

Carbon impregnated with potassium iodide was used as an ozone-scrubbing filter in a chemiluminescence NO_x analyser. When the level of iodide was inadvertently increased to the high level of 40%, the filter exploded violently during replacement after use. This was attributed to oxidation of iodide to iodate by ozone, and frictional initiation of the iodate—carbon mixture when the filter was dismantled.

Citronellic acid

Yost, Y., *Chem. Eng. News*, 1977, **55**(21), 4

During work-up of the products of ozonolysis of *R*- and *S*-citronellic acids, a substantial quantity of the highly explosive trimeric acetone peroxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane) was unwittingly isolated by distillation at 105—135°C to give the solid m.p. 95°C. The peroxide appears to have been produced by ozonolysis of the isopropylidene group in citronellic acid, and presumably the same could occur when any isopropylidene group is ozonised. Appropriate care is advised.

Combustible gases

1. Streng, A. G., *Chem. Abs.*, 1964, **55**, 8862c
2. Nomura, Y. *et al., Chem. Abs.*, 1952, **46**, 4234a

Carbon monoxide and ethylene admitted into contact with ozone via an aluminium tip ignited and burned smoothly, while normal contact of carbon monoxide, nitrogen oxide, ammonia or phosphine causes immediate explosion at 0° or —78°C [1]. At pressures below 10 mbar, contact with ethylene is explosive at —150°C [2].

See Nitrogen oxide, below

trans-2,3-Dichloro-2-butene

1. Griesbaum, K. *et al., J. Amer. Chem. Soc.*, 1976, **98**, 2880
2. Gäb, S. *et al., J. Org. Chem.*, 1984, **49**, 2711—2714

The crude products of ozonolysis at —30°C of the chloroalkene tended to decompose explosively on warming to ambient temperature, particularly in absence of solvents.

The products included the individually explosive compounds acetyl 1,1,-dichloroethyl peroxide, 3,6-dichloro-3,6-dimethyl-2,3,5,6-tetraoxane and diacetyl peroxide [1]. Ozonolysis in ethyl formate saturated with hydrogen chloride gives a high yield of 1,1-dichloroethyl hydroperoxide as a further unstable intermediate product [2].
See OZONIDES

Dicyanogen
Anon., *Chem. Eng. News*, 1957, **35**(21), 22
This hypergolic combination of two extremely endothermic compounds appears to have rocket-propellant capabilities.
See ROCKET PROPELLANTS

Dienes, Oxygen
Griesbaum, K. *et al., Chem. Eng. News*, 1982, **60**(8), 63
Treatment of isoprene, 2,3-dimethylbutadiene or cyclopentadiene in pentane at —78°C with a high ratio ozone/oxygen stream led to immediate ignition and flames in both liquid and gas phases.

Diethyl ether
Mellor, 1941, Vol. 1, 911
Contact of ether with ozonised oxygen produces some of the explosive diethyl peroxide.

1,1-Difluoroethylene
1. Gillies, C. W. *et al., J. Phys Chem.*, 1979, **83**, 1545
2. Agopovich, J. W. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 5049

The product of ozonolysis of 1,1-difluoroethylene is a shock-sensitive peroxidic species [1], which reacts vigorously with aqueous potassium iodide [2].

Ethylene
Mellor, 1941, Vol. 1, 911
Interaction may be explosive, owing to the very low stability of ethylene ozonide.
See Combustible gases, above
See also Ethylene ozonide

Ethylene, Formyl fluoride
Mazur, U. *et al., J. Org. Chem.*, 1979, **44**, 3188
Two attempts to ozonise mixtures of ethylene and formyl fluoride in absence of solvent led to explosions.

Fluoroethylene
See Fluoroethylene ozonide

Hydrogen bromide
Lewis, B. *et al., J. Amer. Chem. Soc.*, 1931, **53**, 3565
Interaction is rapid and becomes explosive above a total pressure of ~40 mbar, even at —104°C.
See Bromine, above

Hydrogen (liquid)
Schwab, G. M., *Umschau*, 1922, 538—539
Liquid hydrogen and solid ozone form very powerfully explosive mixtures.

Hydrogen, Oxygen difluoride
Boehm, R., *Chem. Abs.*, 1975, **83**, 82254
The use of liquid oxygen difluoride (40 or 90%) to stabilise liquid ozone as oxidant for gaseous hydrogen in a rocket motor was not entirely successful, explosions occurring at both concentrations.
See Oxygen fluorides, below

3-Hydroxy-2,2,4-trimethyl-3-pentenoic acid lactone
Perrin, C. L. *et al., J. Org. Chem.*, 1980, **45**, 1706
During work-up after ozonolysis of the lactone to give dimethylmaleic anhydride, removal of excess ozone by a stream of oxygen leads to the precipitation of peroxidic material at the concentration used in the preparation.

4-Hydroxy-4-methyl-1,6-hepatadiene
See 4-Hydroxy-4-methyl-1,6-heptadiene: Ozone

Isopropylidene compounds
See Citronellic acid, above

2-Methyl-1,3-butadiene
See Dienes, above
See also 2-Methyl-1,3-butadiene: Ozone

Nitrogen
Strakhov, B. V. *et al., Chem. Abs.*, 1963, **58**, 5069a
The explosive oxidation of nitrogen in admixture with ozone in metallic vessels has been studied.

Nitrogen oxide
Nomura, Y. *et al., Sci. Reps. Tohoku Univ.*, 1950[A], **2**, 229—232
Violent explosions occurred in mixtures at —189°C.
See Combustible gases, above

Nitrogen trichloride
See Nitrogen trichloride: Initiators

Oxygen fluorides
Streng, A. G., *Chem. Rev.*, 1963, **63**, 613, 619
Mixtures with dioxygen difluoride explode at —148°C, and with ‘dioxygen trifluoride’ (probably mixed dioxygen di- and tetra-fluorides) at —183°C.

Oxygen, Rubber powder
Anon., *Jahresber.*, 1983, 72
In an attempt to introduce carboxyl groups to improve the adhesive properties of rubber, 6 l of powdered rubber (0.1—0.5 mm particle size) in an 8 l flask was treated with ozonised oxygen. The gas stream, containing 5% of ozone was led to the bottom of the flask via a dip tube at the rate of 4 l/min for 2 min, when treatment was

discontinued and the flask closed. After 5 min a violent explosion occurred. This was attributed to formation of ozonides, but exothermic interaction of the high surface area rubber with almost pure oxygen under virtually adiabatic conditions may also have been involved.
See Oxygen: Polymers

Silica gel
Cohen, Z. *et al., J. Org. Chem.*, 1975, **40**, 2142, footnote 6
Silica gel at —78°C adsorbs 4.5 wt% of ozone, and below this temperature the concentration increases rapidly. At below —112°C ozone liquefies and there is a potential explosion hazard at temperatures below —100°C if organic material is present.
See reference 3, main entry

Stibine
Stock, A. *et al., Ber.*, 1905, **38**, 3837
Passage of oxygen containing 2% of ozone through stibine at —90°C caused an explosion. On standing, a suspension of solid stibine in a liquid oxygen solution of ozone eventually exploded, as oxygen evaporated increasing the concentration of ozone and the temperature.

Tetrafluorohydrazine
See Tetrafluorohydrazine: Ozone

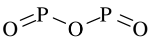
Tetramethylammonium hydroxide
Solomon, I. J. *et al., J. Amer. Chem. Soc.*, 1960, **82**, 5640
During interaction to form tetramethylammonium ozonide, constant agitation and slow ozonisation were necessary to prevent ignition.

Trifluoroethylene
Agopovich, J. W. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 5048
After ozonisation of trifluoroethylene in chlorotrifluoromethane solution at —95°C, the reactor must only be allowed to warm slightly (to —88°C) during subsequent cryogenic distillation. When allowed to warm towards ambient temperature the reactor exploded violently. The residue from distillation is peroxidic and probably sensitive to sudden temperature increases.

Unsaturated acetals
Schuster, L., Ger. Offen. 2 514 001, 1976
Ozonolysis of unsaturated acetals at —70 to 0°C to give glyoxal monoacetals is uneventful in organic solvents, but leads to explosions in aqueous solutions.
See other NON-METALS, OXIDANTS

4841. Phosphorus(III) oxide

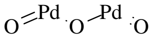
[1314-24-5] **O_3P_2**



See Tetraphosphorus hexaoxide

4842. Palladium(III) oxide

[80680-07-5] **O_3Pd_2**



Sidgwick, 1950, 1573

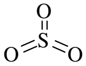
If the hydrated oxide is heated to remove water, it incandesces or explodes, giving the monoxide.

See other METAL OXIDES

See related PLATINUM COMPOUNDS

4843. Sulfur trioxide

[7446-11-9] **O_3S**



HCS 1980, 880

The metastable liquid form boils at 44°C, the more stable solid alpha form melts at 62°C and has 25—30 J/g heat of fusion. This permits pressure generation when proceeding in either direction through the phase change.

Acetonitrile, Sulfuric acid
See Acetonitrile: Sulfuric acid, etc.

Chlorinated solvents
Gilbert E. E. *Chem. Eng. News* 1989 **67**(41) 2
Details of exothermic and gas-evolving reactions are given, storage of such mixtures is not recommended.

Cyclohexanone oxime, Sulfuric acid
See Cyclohexanone oxime: Oleum

Dimethyl sulfoxide
Seel, F., *Inorg. Synth.*, 1947, **2**, 174
Dissolution of sulfur trioxide in the sulfoxide is very exothermic and must be done slowly with cooling to avoid decomposition.

Dimethylformamide
See Sulfur trioxide—dimethylformamide

Dioxane
Sisler, H. H. *et al., Inorg. Synth.*, 1947, **2**, 174
Since the 1:1 addition complex sometimes decomposes violently on storing at ambient temperature, it should only be prepared immediately before use (if refrigerated storage is not possible).

Dioxygen difluoride
See Dioxygen difluoride: Sulfur trioxide

Diphenylmercury
See Diphenylmercury: Chlorine monoxide, etc.

Ethylene oxide
See Ethylene oxide: Pyridine, Sulfur dioxide

Formamide, Iodine, Pyridine
See Formamide: Iodine, etc.

Metal oxides
1. Partington, 1967, 706
2. Mellor, 1941, Vol. 7, 654

The violent interaction with sulfur trioxide causes incandescence with barium oxide [1] and lead oxide [2].

Nitryl chloride
See Nitryl chloride: Inorganic materials

Organic materials, Water
Unremembered suppliers brochure, 1979
Organic materials, particularly if fibrous with adsorbed or absorbed moisture present, may char or ignite in contact with the stabilised liquid form because of the very high heat of hydration (2.1 kJ/g) and formation of hot oleum which then functions as an oxidant.
See other ACID ANHYDRIDES

Other reactants
Yoshida, 1980, 128
MRH values calculated for 18 combinations with various materials are given.

Phosphorus
See Phosphorus: Non-metal oxides

Sulfuric acid
HCS 1980, 702 (65%), 703 (30%), 704 (20%)
Solutions of sulfur trioxide in conc. sulfuric acid (oleum) are available with various proportions of dissolved sulfur trioxide, and the 3 entries in *Handling Chemicals Safely 1980* deal with the properties and hazards of solutions with 65, 30 and 20% of sulfur trioxide, respectively. As expected, the reactivity and oxidising power increase with the content of sulfur trioxide.

Tetrafluoroethylene
1. Anderson, A. W., *Chem. Eng. News*, 1971, **49**(22), 3
2. Xu, B. *et al., Chem. Abs.*, 1982, **97**, 182248
3. Aihara, R. *et al., Chem. Abs.*, 1986, **101**, 99522

Reaction to give tetrafluorooxathietane 2,2-dioxide (tetrafluoroethane sultone) had been used industrially and uneventfully, but reaction with excess sulfur trioxide may cause explosive decomposition to carbonyl fluoride and sulfur dioxide [1]. An incident involving the same explosion hazard was reported 11 years later [2]. Use of inert gas to prevent explosion has been patented [3].

Water

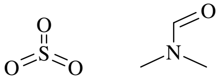
1. Mellor, 1947, Vol. 10, 344
2. Willis, P. B., *Chem. Eng. News*, 1986, **64**(38), 2
3. Eccles, E. J., *Chem. Eng. News*, 1987, **65**(12), 2
4. Rosin, J., *Chem. Eng. News*, 1987, **65**(24), 2

Interaction is vigorously exothermic, sometimes explosive, with evolution of light and heat. A 4:1 mixture of oxide and water completely vaporises, with simultaneous emission of light. Unused portions of ampoules of sulfur trioxide were prepared for disposal by dripping a little water each day during several weeks into the ampoules. When inverted to empty the contents, one such ampoule exploded, scattering conc. sulfuric acid around [2]. This technique probably produces a layer of water above one of conc. sulfuric acid, and when the layers mixed the exotherm burst the narrow-necked ampoule. Moderate quantities of liquid sulfur trioxide (100—500 g) may be disposed of into a strong water stream discharging into an acid-proof drain, using personal protection [3]. It is, however, stressed that all disposal methods involving addition to water are inherently unsafe, because sulfur trioxide is insoluble in water and also highly hydrophobic, so the potential for sudden and violent reaction always exists. The safest method is to dissolve sulfur trioxide in a large volume of conc. sulfuric acid, and then dispose of the weak oleum by slow addition to a large and well stirred volume of water [4].

See other ACID ANHYDRIDES, NON-METAL OXIDES, OXIDANTS

4844. Sulfur trioxide—dimethylformamide

[29584-42-7] **$O_3S.C_3H_7NO$**



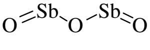
Koch-Light Laboratories Ltd., private comm., 1976

A bottle of the complex exploded in storage. No cause was established, but diffusive ingress of moisture to form sulfuric acid, and subsequent hydrolysis of the solvent with formation of carbon monoxide appear to be possible contributory factors.

See related ACID ANHYDRIDES, NON-METAL OXIDES

4845. Antimony(III) oxide

[1309-64-4] **O_3Sb_2**



HCS 1980, 164

Mellor, 1939, Vol. 9, 425

The powdered oxide ignites on heating in air.

Bromine trifluoride

See Bromine trifluoride: Antimony trichloride oxide

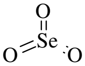
Chlorinated rubber

See CHLORINATED RUBBER: Metal oxides

See other METAL OXIDES

4846. Selenium trioxide

[13768-86-0] **O_3Se**



Organic materials

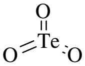
Sorbe, 1968, 124

A powerful oxidant which forms explosive mixtures with organic materials.

See other NON-METAL OXIDES

4847. Tellurium trioxide

[13451-18-8] **O_3Te**



Metals, or Non-metals

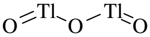
Bailar, 1973, Vol. 2, 971

The yellow α-form is a powerful oxidant, reacting violently when heated with a variety of metallic and non-metallic elements.

See other NON-METAL OXIDES

4848. Thallium(III) oxide

[1314-32-5] **O_3Tl_2**



Sulfur, or Sulfur compounds

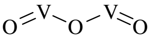
Mellor, 1946, Vol. 5, 434

Mixtures of the oxide with sulfur or antimony trisulfide explode on grinding in a mortar. Dry hydrogen sulfide ignites, and sometimes feebly explodes, over thallium oxide.

See other METAL OXIDES

4849. Vanadium(III) oxide

[1314-34-7] **O_3V_2**

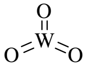


Sidgwick, 1950, 825

It ignites on heating in air.

See other METAL OXIDES

4850. Tungsten(VI) oxide
[1314-35-8] **O_3W**



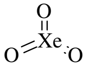
Boron tribromide
See Boron tribromide: Tungsten trioxide

Bromine, Tungsten
See Bromine: Tungsten, etc.

Interhalogens
See Bromine pentafluoride: Acids, etc.
See Chlorine trifluoride: Metals, etc.

Lithium
See Lithium: Metal oxides
See other METAL OXIDES

4851. Xenon trioxide
[13776-58-4] **O_3Xe**



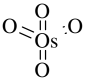
1. Malm, J. G. *et al., Chem. Rev.*, 1965, **65**, 199
2. Chernick, C. L. *et al., J. Chem. Educ.*, 1966, **43**, 619; *Inorg. Synth.*, 1968, **11**, 206, 209
3. Anon., *Chem. Eng. News*, 1963, **41**(13), 45
4. Holloway, J. H., *Talanta*, 1967, **14**, 871—873
5. Shackelford, S. A. *et al., Inorg. Nucl. Chem. Lett.*, 1973, **9**, 609, footnote 9
6. Shackelford, S. A. *et al., J. Org. Chem.*, 1975, **40**, 1869—1875
7. Foropoulos, J. *et al., Inorg. Chem.*, 1982, **21**, 2503—2504

It is a powerful explosive [1] produced when xenon tetrafluoride or xenon hexafluoride are exposed to moist air and hydrolysed. Some tetrafluoride is usually present in xenon difluoride, so the latter is potentially dangerous. Although safe to handle in small amounts in aqueous solution, great care must be taken to avoid solutions drying out, e.g. around ground stoppers [2]. Full safety precautions have been discussed [2,3,4]. Precautions necessary for use of aqueous solutions of the trioxide as an epoxidation reagent are detailed [5,6]. A safe method of preparation, so far free from explosions, from xenon hexafluoride and difluorophosphoric acid at 0°C has been described [7].

See other NON-METAL OXIDES, OXIDANTS, XENON COMPOUNDS

4852. Osmium(VIII) oxide

[20816-12-0] **O_4Os**



Hydrogen peroxide

See Hydrogen peroxide: Metals, etc.

1-Methylimidazole

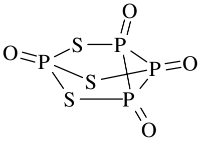
Nielsen, A. J., *J. Chem. Soc., Dalton Trans.*, 1979, 1084—1088

An explosion occurred when the oxidant was added to the imidazole.

See other METAL OXIDES, OXIDANTS

4853. Tetraphosphorus tetraoxide trisulfide

[ ] **$O_4P_4S_3$**



Water

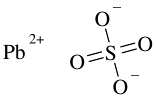
Mellor, 1971, Vol. 8, Suppl. 3, 435

It ignites if moistened with water.

See related NON-METAL OXIDES, NON-METAL SULFIDES

4854. Lead sulfate

[7446-14-2] **O_4PbS**



Potassium

See Potassium: Oxidants

See other METAL OXONON-METALLATES

4855. Dilead(II)lead(IV) oxide

[1314-41-6] **O_4Pb_3**

$O{=}Pb{=}O \qquad Pb{=}O \qquad Pb{=}O$

HCS 1980, 808

Dichloromethylsilane

See Dichloromethylsilane: Oxidants

Eosin lead salts

Anon., *Chem. & Ind.*, 1995, (22), 912

The mixture of the lead salts of eosin and red lead formerly used as a pigment, proved to be a very easily ignited pyrotechnic mix.

Peroxyformic acid

See Peroxyformic acid: Metals, etc.

Seleninyl chloride

See Seleninyl chloride: Metal oxides

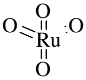
2,4,6-Trinitrotoluene

See 2,4,6-Trinitrotoluene: Added impurities

See other METAL OXIDES, OXIDANTS

4856. Ruthenium(VIII) oxide

[20427-56-9] **O_4Ru**



1. Mellor, 1942, Vol. 15, 520
2. Brauer, 1965, Vol. 2, 1600
3. Bailar, 1973, Vol. 3, 1194
4. Ullmann, 1992, Vol. A21, 125/6

The liquid (which shows no true b.p.) is said to decompose explosively either above 106° or above 180°C [1,2,3]. The oxide should not be stored in bulk, either as liquid or solid [4].

Ammonia

Watt, J., *J. Inorg. Nucl. Chem.*, 1965, **27**, 262

Rapid interaction at —70°C/1 mbar causes ignition. Slow interaction produced a solid which exploded at 206°C, probably owing to formation of ruthenium amide oxide or ruthenium nitride.

Hydriodic acid

Mellor, 1942, Vol. 15, 520

Reaction with the acid to give ruthenium triiodide is explosively violent.

Organic materials

1. Mellor, 1942, Vol. 15, 517, 520
2. Brauer, 1965, Vol. 2, 1600

The solid oxide, or its concentrated solutions or vapour, tends to oxidise ethanol, cellulose fibres, etc., explosively [1,2]. Ethanol also gives an explosive by-product, probably an organoruthenium derivative [1].

Phosphorus tribromide

Mellor, 1971, Vol. 8, Suppl. 3, 521

Interaction is vigorously exothermic.

Sulfur

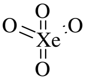
Mellor, 1942, Vol. 15, 520

The vapour explodes in contact with sulfur.

See other METAL OXIDES, OXIDANTS

4857. Xenon tetraoxide

[12340-14-6] **O_4Xe**



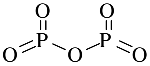
1. Selig, H. *et al., Science* (New York), 1964, **143**, 1322
2. Gerken, M. *et al., Inorg. Chem.*, 2002, **41**(2), 198

Decomposition may be explosive, even at —40°C [1]. Solutions stable at —30°C can be formed in hydrogen fluoride, bromine pentafluoride and chlorosulfonyl fluoride. But melting solvents onto solid xenon tetroxide at —196 C often causes explosions if performed too rapidly [2].

See other NON-METAL OXIDES, OXIDANTS, XENON COMPOUNDS

4858. Phosphorus(V) oxide

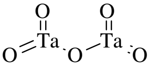
[1314-56-3] **O_5P_2**



See Tetraphosphorus decaoxide

4859. Tantalum(V) oxide

[1314-61-0] **O_5Ta_2**



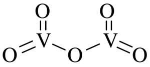
Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

See other METAL OXIDES

4860. Vanadium(V) oxide

[1314-62-1] **O_5V_2**



HCS 1980, 950

Calcium, Sulfur

491M, 1975, 81

A mixture of the metal and oxidant, contaminated with sulfur and some water, led to a serious fire.

Chlorine trifluoride

See Chlorine trifluoride: Metals, etc.

Lithium MRH 2.43/7

See Lithium: Metal oxides

Other reactants

Yoshida, 1980, 118

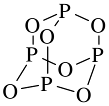
MRH values calculated for 9 combinations, largely with oxidisable materials, are given.

Peroxyformic acid MRH 5.69/99+

See Peroxyformic acid: Metals, etc.

See other METAL OXIDES, OXIDANTS

4861. Tetraphosphorus hexaoxide (Phosphorus(III) oxide)
[10248-58-5] O_6P_4



Ammonia

Thorpe, T. E. *et al., J. Chem. Soc.*, 1891, **59**, 1019

Interaction of the molten oxide and ammonia under nitrogen is rather violent and the mixture ignites. Use of a solvent and cooling controls the reaction to produce diamidophosphinic acid.

Borane

See Octaphosphorus dodecaoxide bis(borane)

Disulfur dichloride

Mellor, 1940, Vol. 8, 898

Interaction is very violent.

Halogens

1. Thorpe, T. E. *et al., J. Chem. Soc.*, 1891, **59**, 1019
2. Mellor, 1940, Vol. 8, 897

The oxide ignites in contact with excess chlorine gas [1], and reacts violently, usually igniting, with liquid bromine [2].

Organic liquids

1. Thorpe, T. E. *et al., J. Chem. Soc.*, 1890, **57**, 569—573
2. Mellor, 1971, Vol. 8, Suppl. 3, 382

The oxide ignites immediately with ethanol at ambient temperature [1]. The liquid oxide (above 24°C) reacts very violently with methanol, dimethylformamide, dimethyl sulfite or dimethyl sulfoxide (also with arsenic trifluoride) and charring may occur [2].

Oxygen

Mellor, 1940, Vol. 8, 897—898; 1971, Vol. 8, Suppl. 3, 380—381

Interaction with air or oxygen is rapid and, at slightly elevated temperatures in air or at high concentration of oxygen, ignition is very probable, particularly if the oxide is molten (above 22°C) or distributed as a thin layer. The solid in contact with oxygen at 50—60°C ignites and burns very brilliantly. During distillation of phosphorus(III) oxide, air must be rigorously excluded to avoid the possibility of explosion. The later reference states that the carefully purified oxide does not ignite in oxygen, and that the earlier observations were on material containing traces of white phosphorus.

Phosphorus pentachloride

See Phosphorus pentachloride: Phosphorus(III) oxide

Sulfur

1. Thorpe, T. E. *et al., J. Chem. Soc.*, 1891, **59**, 1019
2. Pernert, J. C. *et al., Chem. Eng. News*, 1949, **27**, 2143

Interaction of a mixture of sulfur and the oxide under inert atmosphere above 160°C to form tetraphosphorus hexaoxide tetrasulfide is violent and dangerous on scales of working other than small [1]. A safer procedure involving distillation of phosphorus(V) oxide and phosphorus(V) sulfide is described [2].

Sulfuric acid

Mellor, 1940, Vol. 8, 898

Addition of sulfuric acid to the oxide causes violent oxidation, and ignition if more than 1—2 g is used.

Water

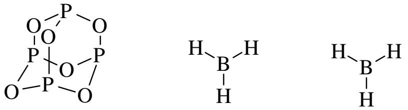
Mellor, 1940, Vol. 8, 897

Reaction with cold water is slow, but with hot water, violent, the evolved phosphine igniting. With more than 2 g of oxide, violent explosions occur.

See other NON-METAL OXIDES, REDUCANTS

4862. Tetraphosphorus hexaoxide—bis(borane)

[14940-94-4] **$O_6P_4.B_2H_6$**



Water

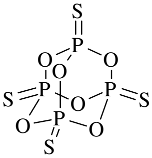
Mellor, 1971, Vol. 8, Suppl. 3, 382

The compound ignites in contact with a little water.

See related BORANES, NON-METAL OXIDES

4863. Tetraphosphorus hexaoxide tetrasulfide

[15780-31-1] **$O_6P_4S_4$**



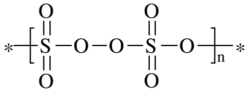
Preparative hazard

See Tetraphosphorus hexaoxide: Sulfur

See related NON-METAL OXIDES, NON-METAL SULFIDES

4864. Disulfur heptaoxide

[12065-85-9] **O_7S_2**



$$*\!-\!\left[\!-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-\right]_n\!-*$$

Meyer, F. *et al., Ber.*, 1922, **55**, 2923

The crystalline material (‘peroxydisulfuric anhydride’, of unknown structure) soon explodes on exposure to moist air.

See other ACID ANHYDRIDES, NON-METAL OXIDES

4865. Triuranium octaoxide

[1344-59-8] **O_8U_3**

U_3O_8

Barium oxide

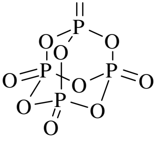
Mellor, 1942, Vol. 12, 49

Interaction below 300°C is vigorous and very exothermic.

See other METAL OXIDES

4866a. Tetraphosphorus decaoxide (Phosphorus(V) oxide)

[16752-60-6] **$O_{10}P_4$**



(*MCA SD-28*, 1948); *HCS 1980*, 747

Barium sulfide

See Barium sulfide: Phosphorus(V) oxide

Formic acid MRH 0.29/99+

See Formic acid: Phosphorus pentaoxide

Hydrogen fluoride

Gore, G., *J. Chem Soc.*, 1869, **22**, 368

Interaction is vigorous below 20°C.

Inorganic bases

1. Mellor, 1940, Vol. 8, 945
2. Van Wazer, 1958, Vol. 1, 279

Dry mixtures with calcium or sodium oxides do not react in the cold, but interact violently if warmed or moistened, evolving phosphorus(V) oxide vapour [1]. A mixture of the oxide and sodium carbonate may be initiated by strong local heating, when the whole mass will suddenly become hot [2].

Iodides

Pascal, 1960, Vol. 16.1, 538

Interaction is violent

Metals MRH Aluminium 4.89/39, magnesium 5.48/45

Mellor, 1940, Vol. 8, 945

Interaction with warm sodium or potassium is incandescent and explosive with heated calcium.

Methyl hydroperoxide

See Methyl hydroperoxide: Alone, etc.

Other reactants

Yoshida, 1980, 119

MRH values calculated for 5 combinations with other materials are given.

Oxidants

See Bromine pentafluoride: Acids, etc.

See Chlorine trifluoride: Metals, etc.

See Hydrogen peroxide: Phosphorus(V) oxide

See Oxygen difluoride: Phosphorus(V) oxide

See Perchloric acid: Dehydrating agents

3-Propynol

See 3-Propynol: Phosphorus pentaoxide

Water

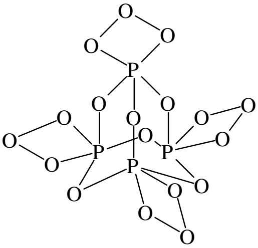
1. Mellor, 1940, Vol. 8, 944
2. *MCA SD-28*, 1948

Phosphorus(V) oxide is a very powerful desiccant and its interaction with liquid water is very energetic and highly exothermic [1]. The increase in temperature may be enough to ignite combustible materials if present and in contact [2].

See other ACID ANHYDRIDES, NON-METAL OXIDES

4866b. Tetraphosphorus octadecaoxide (Tetraspiro[2,4,6,8,9,10-hexaoxa-1,3,5,7tetraphospotriccyclo[3.3.1.13,7]decane-1,4‘λ5:3,4’’λ5:5,4’’’λ5:7,4’’’’λ5:-tetrakistrioxaphosphetane])

[581789-81-3] **$O_{18}P_4$**



1. Meisel, M. *et al., Angew. Chem. (Int.)*, 2003, **42**(22), 2484
2. Klapötke, T. M., *Angew. Chem. (Int.)*, 2003, **42**(30), 3461

This triozonide, prepared from phosphorus trioxide, decomposes from 35°C in solution evolving oxygen. The solid, isolable at —78°C, tends to explode on heating.
See other OZONIDES

4867. Osmium

[7440-04-2] **Os**

Os

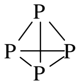
Chlorine trifluoride
See Chlorine trifluoride: Metals

Fluorine
See Fluorine: Metals

Phosphorus
See Phosphorus: Metals
See other METALS

†4868. Phosphorus

[7723-14-0] **P**



(*MCA SD-16*, 1947); *FPA H19*, 1973; *HCS 1980*, 748 (red), 750 (white); *RSC Lab. Hazard Data Sheet No. 79*, 1989 (white P)

1. Albright and Wilson, (Manufacturer’s safety sheet)
2. Anon., *Chem. Trade J.*, 1936, **98**, 522
3. Anon., *CISHC Chem. Safety Summ.*, 1974—1975, **45—46**, 3
4. Anon., *Jahresber.*, 1979, 73

5. Anon., *Fire Prev.*, 1987, (197), 42—43
6. Anon., *Fire Prevention*, 1992, (249), 45

White phosphorus has an autoignition temperature only slightly above ambient, dispersed it will soon heat itself to that by the slow oxidation responsible for its glow. Red is not spontaneously combustible, however if it does catch fire white will be produced, so that the fire, once extinguished, may spontaneously re-ignite. Both can produce phosphine, among other products, by slow reaction with water. Sealed containers of damp phosphorus (white is often stored under water) may pressurise with highly toxic, pyrophoric, gas mixtures [1].

Red phosphorus powder being charged into a reaction vessel exploded when the lid of the tin fell in and was struck by the agitator [2]. A further case of ignition of red phosphorus by impact from its metal container is reported [3]. Impact of a rubber hammer on a nitrogen-purged stirred metal feed container of red phosphorus powder led to ignition and a jet of flame [4]. A rail tanker containing 44 kl of molten white phosphorus at about 50°C was damaged in a derailment, and the contents on exposure to ambient air immediately ignited, and burned for 5 days before being brought under control [5]. A very similar rail tankwagon fire occurred a few years later [6].

See Oxygen, below

See other FRICTIONAL INITIATION INCIDENTS

Alkalies

Mellor, 1940, Vol. 8, 802

Contact of phosphorus with boiling caustic alkalies or with hot calcium hydroxide evolves phosphine, which usually ignites in air.

Chlorosulfuric acid MRH 2.51/75

Heumann, K. *et al., Ber.*, 1882, **15**, 417

White phosphorus begins to reduce the acid at 25—30°C and the vigorous reaction accelerates to explosion. Red phosphorus is similar at a higher initial temperature.

Cyanogen iodide

Mellor, 1940, Vol. 8, 791

Molten phosphorus reacts incandescently.

Halogen azides

See HALOGEN AZIDES: METALS, OR PHOSPHORUS

Halogen oxides MRH values show % of oxidant

See Chlorine dioxide: Non-metals MRH 7.87/73

Dichlorine oxide: Oxidisable materials MRH 0.92/92

Oxygen difluoride: Non-metals

Trioxygen difluoride: Various materials

Halogens, or Interhalogens MRH Chlorine 1.92/85

1. Mellor, 1940, Vol. 8, 785; 1956, Vol. 2, Suppl. 1, 379
2. Christomanos, A. C., *Z. Anorg. Chem.*, 1904, **41**, 279
3. Kuhn, R. *et al., Helv. Chim. Acta*, 1928, **11**, 107
4. Newkome, G. R. *et al., J. Chem. Soc., Chem. Comm.*, 1975, 885—886

Both yellow and red phosphorus ignite on contact with fluorine and chlorine; red ignites in liquid bromine or in a heptane solution of chlorine at 0°C. Yellow phosphorus explodes in liquid bromine or chlorine, and ignites in contact with bromine vapour or solid iodine [1]. Interaction of bromine and white phosphorus in carbon disulfide gives a slimy by-product which explodes violently on heating [2]. Interaction of phosphorus and iodine in carbon disulfide is rather rapid [3]. A less hazardous preparation of diphosphorus tetraiodide from phosphorus trichloride and potassium iodide in ether is recommended [4].

See Bromine pentafluoride: Acids, etc.
See Bromine trifluoride: Halogens, etc.
See Chlorine trifluoride: Metals, etc.
See Iodine pentafluoride: Metals, etc.
See Iodine trichloride: Phosphorus

Hexalithium disilicide
Mellor, 1940, Vol. 6, 169
Interaction is incandescent.

Hydriodic acid
1. Blau, K., private comm., 1965
2. Agranat, I. *et al., J. Chem. Soc., Perkin Trans. 1*, 1974, 1159
3. Villain, F. J. *et al., J. Med. Chem.*, 1964, **7**, 457, footnote 9

During removal of free iodine from hydriodic acid by distillation from red phosphorus, phosphine was produced. When air was admixed by changing the receiver flask, an explosion occurred. Omission of distillation by boiling the reactants in inert atmosphere, and separating the phosphorus by fitration through a sintered glass funnel containing solid carbon dioxide gave a colourless product [1]. Potential hazards incidental to the use of red phosphorus and hydriodic acid as a reducing agent for organic carbonyl compounds have been noted. Accumulation in a reflux condenser of phosphonium iodide which will react violently with water [2], and 2 unexplained explosions [3], possibly owing to the same cause, have been reported.
See Phosphonium iodide

Hydrogen peroxide MRH 7.78/73
See Hydrogen peroxide: Phosphorus

Magnesium perchlorate
1965 Summary of Serious Accidents, Washington, USAEC, 1966
Phosphorus and magnesium perchlorate exploded violently while being mixed. It seems likely that this was initiated by interaction of phosphorus and traces of perchloric acid to form magnesium phosphate. The acid may have been present as impurity in the magnesium perchlorate, or might have been formed from traces of phosphoric acid in the phosphorus. Once formed, the perchloric acid would be rendered anhydrous by the powerful dehydrating action of magnesium perchlorate.

Metal acetylides
Mellor, 1946, Vol. 5, 848—849

Monorubium acetylide and monocaesium acetylide incandesce with warm phosphorus. Lithium acetylide and sodium acetylide burn vigorously in phosphorus vapour, and the potassium, rubidium and caesium analogues should react with increasing violence.

Metal halides

Mellor, 1939, Vol. 9, 467; 1943, Vol. 11, 234

Phosphorus ignites in contact with antimony pentachloride and explodes with chromyl chloride in presence of moisture at ambient temperature.

Metal halogenates MRH values below references

Mellor, 1941, Vol. 2, 310; 1940, Vol. 8, 785—786

MRH Barium chlorate 5.06/83, calcium chlorate 5.61/77, potassium chlorate 6.07/76, sodium bromate 4.98/80, sodium chlorate 7.32/75, zinc chlorate 6.11/76

Dry finely divided mixtures of red (or white) phosphorus with chlorates, bromates or iodates of barium, calcium, magnesium, potassium, sodium or zinc will readily explode on initiation by friction, impact or heat. Fires have been caused by accidental contact in the pocket between the red phosphorus in the friction strip on safety-match boxes and potassium chlorate tablets. Addition of a little water to a mixture of white or red phosphorus and potassium iodate causes a violent or explosive reaction. Addition of a little of a solution of phosphorus in carbon disulfide to potassium chlorate causes an explosion when the solvent evaporates. The extreme danger of mixtures of red phosphorus (or sulfur) with chlorates was recognised in the UK some 50 years ago when unlicenced preparation of such mixtures was prohibited by Orders in Council.

Metal oxides or peroxides MRH values below references

Mellor, 1941, Vol. 2, 490; Vol. 7, 690; 1940, Vol. 8, 792; 1943, Vol. 11, 234

MRH Chromium trioxide 3.68/84, lead peroxide 1.30/90, potassium peroxide 5.90/81, sodium peroxide 2.30/86

Red phosphorus reacts vigorously on heating with copper oxide or manganese dioxide; and on grinding with lead oxide, mercury oxide or silver oxide, ignition may occur. Red phosphorus ignites in contact with lead peroxide, potassium peroxide or sodium peroxide, while white phosphorus explodes, and also in contact with molten chromium trioxide at 200°C.

Metal sulfates

Berger, E., *Compt. rend.*, 1920, **170**, 1492

Excess red phosphorus will burn admixed with barium or calcium sulfates if primed at a high temperature with potassium nitrate—calcium silicide mixture.

See Potassium nitrate: Calcium silicide

Metals

1. Mellor, 1941, Vol. 7, 115; 1940, Vol. 8, 842, 847, 853; 1971, Vol. 8, Suppl. 3, 228
2. Van Wazer, 1958, Vol. 1, 159
3. Mellor, 1942, Vol. 15, 696; 1937, Vol. 16, 160
4. Iseler, G. W. *et al., Int. Conf. Indium Phosphide Relat. Mater.*, 1992, 266

Reaction of beryllium, copper, manganese, thorium or zirconium is incandescent when heated with phosphorus [1] and that of cerium, lanthanum, neodymium and

praseodymium is violent above 400°C [2]. Osmium incandesces in phosphorus vapour, and platinum burns vividly below red-heat [3]. Red phosphorus shows very variable vapour pressure between batches (not surprising, it is an indeterminate material). This leads to explosions when preparing indium phosphide by reactions involving fusion with phosphorus in a sealed tube [4].
See Aluminium: Non-metals

Nitrates
MRH Ammonium nitrate 4.60/86, potassium nitrate 3.14/73, silver nitrate 3.89/82, sodium nitrate 4.43/73
1. Mellor, 1941, Vol. 3, 470; 1940, Vol. 4, 987; Vol. 8, 788
2. Anon., *Jahresber.*, 1975, 83—84

Yellow phosphorus ignites in molten ammonium nitrate, and mixtures of phosphorus with ammonium nitrate, mercury(I) nitrate or silver nitrate explode on impact. Red phosphorus is oxidised vigorously when heated with potassium nitrate [1]. During development of new refining agents for aluminium manufacture, a mixture containing red phosphorus (16%) and sodium nitrate (35%) was being pressed into 400 g tablets. When the die pressure was increased to 70 bar, a violent explosion occurred [2].

Nitric acid MRH 7.66/67
See Nitric acid: Non-metals

Nitrogen halides
See Nitrogen tribromide hexaammoniate: Initiators
Nitrogen trichloride: Alone, or Non-metals MRH 3.35/87

Nitrosyl fluoride
See Nitrosyl fluoride: Metals, etc.

Nitryl fluoride
See Nitryl fluoride: Non-metals

Non-metal halides
1. Pascal, 1960, Vol. 13.2, 1162
2. Mellor, 1946, Vol. 5, 136; 1940, Vol. 8, 787; 1947, Vol. 10, 906

Either the white or red form incandesces with boron triiodide [1]. Red phosphorus incandesces in seleninyl choride while white explodes. Red phosphorus reacts vigorously on warming with sulfuryl chloride or disulfuryl chloride, and violently with disulfur dibromide [2].

Non-metal oxides MRH Dinitrogen tetraoxide 9.12/65
Mellor, 1940, Vol. 8, 786—787
Warm or molten white phosphorus burns vigorously in nitrogen oxide, dinitrogen tetraoxide or dinitrogen pentaoxide. White phosphorus ignites after some delay in contact with the vapour of sulfur trioxide, but immediately in contact with the liquid if a large portion is used.

Other reactants
Yoshida, 1980, 73—75
MRH values calculated for 36 combinations, largely with oxidants, are given.

Oxidants

Inoue, Y. *et al., Chem. Abs.*, 1988, **108**, 134435

Impact sensitivities of mixtures of red phosphorus with various oxidants were determined in a direct drop-ball method, which indicated higher sensitivities than those determined with an indirect striker mechanism. Mixtures with silver chlorate were most sensitive, those with bromates, chlorates and chlorites were extremely sensitive, and mixtures with sodium peroxide and potassium superoxide were more sensitive than those with barium, calcium, magnesium, strontium or zinc peroxides. Mixtures with perchlorates or iodates had sensitivities comparable to those of unmixed explosives, such as lead azide, 3,5-dinitrobenzenediazonium-2-oxide etc.

Oxygen

1. Mellor, 1940, Vol. 8, 771
2. Van Wazer, 1958, 1, 97
3. Mellor, 1971, Vol. 8, Suppl. 3, 237—245

The reactivity of phosphorus with air or oxygen depends on the allotrope of phosphorus involved and the conditions of contact, white (yellow) phosphorus being by far the more reactive. White phosphorus readily ignites in air if warmed, finely divided (e.g. from an evaporating solution) or under conditions where the slow oxidative exotherm cannot be dissipated. Contact with finely divided charcoal or lampblack promotes ignition, probably by adsorbed oxygen [1]. Contact with amalgamated aluminium also promotes ignition [2]. Oxidation of phosphorus under both explosive and non-explosive conditions has been reviewed in detail [3].

Peroxyformic acid MRH 6.65/72

See Peroxyformic acid: Non-metals

Potassium nitride

Mellor, 1940, Vol. 8, 99

Potassium and other alkali-metal nitrides react on heating with phosphorus to give a highly flammable mixture which evolves ammonia and phosphine with water.

Potassium permanganate MRH 2.34/84

Mellor, 1942, Vol. 12, 322

Grinding mixtures of phosphorus and potassium permanganate causes explosion, more violent if also heated.

Selenium

See Selenium: Phosphorus

Sodium chlorite MRH 6.23/79

See Sodium chlorite: Phosphorus

Sulfur

See Sulfur: Non-metals

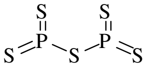
Sulfuric acid MRH 2.64/72

See Sulfuric acid: Phosphorus

See other NON-METALS, PYROPHORIC MATERIALS

4869. Phosphorus(V) sulfide

[1314-80-3] **P_2S_5**



See Tetraphosphorus decasulfide

4870. Zinc phosphide

[1314-84-7] **P_2Zn_3**

Zn^{2+} Zn^{2+} Zn^{2+} P^{3-} P^{3-}

Perchloric acid

See Perchloric acid: Zinc phosphide

Water

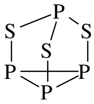
Fehse, W., *Feuerschutz*, 1938, **18**, 17

Contact of one drop of water with a zinc phosphide rodenticide preparation caused ignition.

See other METAL NON-METALLIDES

4871. Tetraphosphorus trisulfide

[1314-85-8] **P_4S_3**



Gibson, 1969, 118—119

It ignites in air above 100°C.

Other reactants

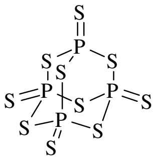
Yoshida, 1980, 131

MRH values calculated for 16 combinations, largely with oxidants, are given.

See other NON-METAL SULFIDES

4872. Tetraphosphorus decasulfide (Phosphorus(V) sulfide)

[15857-57-5] **P_4S_{10}**



1. (*MCA SD-71*, 1958)
2. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
3. Albright and Wilson, (Manufacturer's safety sheet)

The general reactivity of the sulfide depends markedly on the physical form, and differences of a factor of 10 may be involved. It is ignitable by friction, sparks or flames, and ignites in dry air if heated close to the m.p., 275—280°C. The dust (200 mesh) forms explosive mixtures in air above a concentration of 0.5% w/v [1], and maximum explosion pressures of 4.35 bar, with maximum rate of rise exceeding 680 bar/s have been determined [2]. The dust can acquire sufficient static electricity from movement for ignition to occur [3].

Alcohols

1. *MCA Case History No. 227*
2. Ashford, J. S., private comm., 1964

A mixture of the sulfide, ethylene glycol and hexane in a mantle-heated flask spontaneously overheated and exploded at an internal temperature of around 180°C. It had been intended to maintain the reaction temperature at 60°C, but since alcoholysis of the sulfide is exothermic, presence of the heating mantle prevented the dissipation of heat, and the reaction accelerated continuously until explosive decomposition occurred [1]. An incident in similar circumstances involving interaction of the sulfide with 4-methyl-2-pentanol also led to violent eruption of the flask contents.

Diethyl maleate, Methanol

Nolan, 1983, Case history 152

In manufacture of Malathion, the phosphorus sulfide dissolved in toluene is treated first with methanol, then diethyl maleate. Use of insufficient toluene to dissolve the sulfide led to a runaway exothermic reaction and explosion.

See Alcohols, above

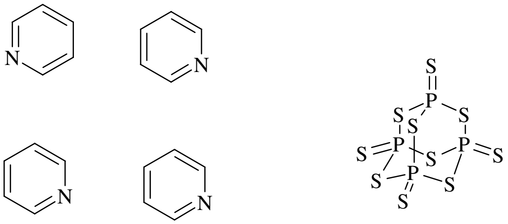
Water

Haz. Chem. Data, 1975, 239

It heats and may ignite in contact with limited amounts of water, hydrogen sulfide also being evolved.

See other NON-METAL SULFIDES

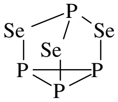
4873. Tetraphosphorus decasulfide . pyridine complex
[71257-31-3] **$P_4S_{10}.4C_5H_5N$**



Riedel-de Haën catalogue, 1986

Although convenient to handle, the complex is classed as highly flammable.
See related NON-METAL SULFIDES

4874. Tetraphosphorus triselenide
[1314-86-9] **P_4Se_3**



1. Mellor, 1947, Vol. 10, 790
2. Stoppioni, P. *et al., Gazz. Chim. Ital.*, 1988, **118**, 581—582

It ignites when heated in air [1]. A new and safer synthesis from red phosphorus and grey selenium has been described [2].
See related NON-METAL SULFIDES

4875. Lead pentaphosphide
[ ] **P_5Pb**

PbP_5

Bailar, 1973, Vol. 2, 117
It ignites in air
See other METAL NON-METALLIDES, PYROPHORIC MATERIALS

4876. Lead
[7439-92-1] **Pb**

Pb

HCS 1980, 534 (powder)

Mézáros, L., *Tetrahedron Lett.*, 1967, 4951
The finely divided lead produced by reduction of the oxide with furfural vapour at 290°C is pyrophoric and chemically reactive.

Hydrogen peroxide, Trioxane
See Hydrogen peroxide: Lead, Trioxane

Nitric acid, Rubber
See Nitric acid: Lead-containing rubber

Oxidants
See Chlorine trifluoride: Metals
Hydrogen peroxide: Metals
Ammonium nitrate: Metals

Sodium acetylide
See Sodium acetylide: Metals
See other METALS, PYROPHORIC METALS

4877. Lead—tin alloys

[12333-97-0] (1:1 alloy) Pb—Sn

Pb——Sn

Palm oil, Steel sheets

Nedelcu, C. *et al.*, Rom. Pat. 68 602, 1979

The explosion hazards associated with use of palm oil when coating steel sheets with molten alloys (8—12% tin)is eliminated by use of molten sodium acetate in place of the oil.

See other ALLOYS

4878. Lead—zirconium alloys

[12412-94-1] (3:5 alloy) Pb—Zr

Pb——Zr

Alexander, P. P., US Pat. 2 611 316. 1952

Alloys containing 10—70% of zirconium will pulverise and ignite on impact.

See other ALLOYS, PYROPHORIC ALLOYS

4879. Palladium

[7440-05-3] Pd

Pd

Finely divided palladium (palladium-black) used as a hydrogenation catalyst is usually pyrophoric and needs appropriate handling precautions.

Aluminium

See Aluminium: Catalytic metals

Arsenic

See Arsenic: Metals

Carbon

1. Mozingo, R., *Org. Synth.*, 1955, Coll. Vol. 3, 687
2. Rachlin, A. I. *et al., Org. Synth.*, 1971, **51**, 687
3. Fraser, R., private comm., 1973

Palladium-on-carbon catalysts prepared by formaldehyde reduction are less pyrophoric than those reduced with hydrogen [1]. Such catalysts become extremely pyrophoric on thorough vacuum drying [2]. Those prepared on high surface-area supports (up to 2000 m^2/g) are highly active and readily will cause catalytic ignition of hydrogen—air or solvent—air mixtures. Methanol is noted for easy ignition because of its high volatility [3].

Formic acid

See Formic acid: Palladium—carbon catalyst

Hydrogen, Hydrogen peroxide
See Hydrogen peroxide: Hydrogen, Palladium

Hydrogen, Poly(tetrafluoroethylene)
See Poly(tetrafluoroethylene): Metal hydrides

Ozonides
See OZONIDES (reference 4)

Sodium tetrahydroborate
Augustine, 1968, 75
In preparation for the reduction of a nitro compound, the tetrahydroborate solution is added to an aqueous supension of palladium-on-charcoal catalyst. The reversed addition of dry catalyst to the tetrahydroborate solution may cause ignition of liberated hydrogen.

Sulfur
See Sulfur: Metals
See other HYDROGENATION CATALYSTS, METALS, PYROPHORIC METALS

4880. Praseodymium
[7440-10-0] **Pr**

Pr

Bromine
See Bromine: Metals,
See also LANTHANIDE METALS
See other METALS

4881. Platinum
[7440-06-4] **Pt**

Pt

1. van Campen, M. G., *Chem. Eng. News*, 1954, **32**, 4698
2. Tilford, C. H., private comm., 1965

Finely divided (catalytic) forms of platinum are hazardous to handle if allowed to dry. Used Adams' hydrogenation catalyst exploded while being sieved in air. It had been well washed, finally with water, and then air dried [1]. Manipulation of used catalyst on filter paper caused a violent explosion [2]. The explosive catalysed oxidation of adsorbed hydrogen is suspected here.
See Zinc: Catalytic metals

Acetone, Nitrosyl chloride
See Nitrosyl chloride: Acetone, etc.

Aluminium
See Aluminium: Catalytic metals

Arsenic

Wöhler, L., *Z. Anorg. Chem.*, 1930, **186**, 324

During interaction to give platinum diarsenide in a sealed tube at 270°C, the highly exothermic reaction may burst the tube.

Carbon, Methanol

Unpublished information, 1982

Ignition occurred when methanol was charged into an unpurged autoclave containing platinum-on-carbon catalyst.

Dioxygen difluoride

See Dioxygen difluoride: Various materials

Ethanol

Elkins, J. S., private comm., 1968

Addition of platinum-black catalyst to ethanol caused ignition. Pre-reduction with hydrogen and/or nitrogen purging of air prevented this.

Hydrazine

See Hydrazine: Metal catalysts

Hydrogen peroxide

See Hydrogen peroxide: Metals

Hydrogen, Air

Coleman, J. W., private comm., 1965

A platinised alumina catalyst had been treated with flowing hydrogen at ambient temperature. Purging with air caused an explosion. Inert gas purging is essential after treating catalysts or adsorbent with hydrogen before admitting air.

Lithium

Nash, C. P., *Chem. Eng. News*, 1961, **39**(5), 42

Interaction to form an intermetallic compound sets in violently at 540°C±20°C.

Methyl hydroperoxide

See Methyl hydroperoxide: Alone, etc.

Ozonides

See OZONIDES (reference 4)

Peroxomonosulfuric acid

See Peroxomonosulfuric acid: Catalysts

Phosphorus

See Phosphorus: Metals

Selenium, or Tellurium

Mellor, 1937, Vol. 16, 158

Finely divided or spongy platinum reacts incandescently when heated with selenium or tellurium.

Vanadium dichloride, Water

See Vanadium dichloride: Platinum, Water

See other HYDROGENATION CATALYSTS, METALS, PYROPHORIC METALS

4882. Plutonium

[7440-07-5] **Pu**

Pu

1. Bailar, 1973, Vol. 5, 44—45
2. Williamson, G. K., *Chem. & Ind.*, 1960, 1384

The reactive metal is pyrophoric in air at elevated temperatures; lathe turnings have ignited at 265°C and 140-mesh powder at 135°C [1]. This most extremely toxic metal may be worked under nitrogen, argon, or helium (but not carbon dioxide) at temperatures above 600°C [2].

Carbon tetrachloride

Serious Accid. Series, No. 246, Washington, USAEC, 1965

While draining after degreasing in the solvent, plutonium chips ignited, and when accidentally dropped into the solvent, caused an explosion.

See other METAL—HALOCARBON INCIDENTS

Water

MCA Case History No. 1212

Plutonium components, normally kept under argon, were accidentally exposed to air and moisture, probably forming plutonium hydride and hydrated oxides. When the plastics containing bag was disturbed, ignition occurred, causing widespread radiation contamination.

See Plutonium(III) hydride

See other METALS, PYROPHORIC METALS

4883. Rubidium

[7440-17-7] **Rb**

Rb

Mellor, 1941, Vol. 2, 468; 1963, Vol. 2, Suppl. 2.2, 2172

Rubidium is a typical but very reactive member of the series of alkali metals.It is appreciably more reactive than potassium, but less so than caesium, and so would be expected to react more violently with those materials that are hazardous with potassium or sodium. Rubidium ignites on exposure to air or dry oxygen, largely forming the oxide.

Halogens

Mellor, 1941, Vol. 2, 13; 1963, Vol. 2, Suppl. 2.2, 2174

Ignition occurs in fluorine, chlorine and bromine or iodine vapours. Contact with liquid bromine would be expected to cause a violent explosion.

Mercury

Mellor, 1941, Vol. 2, 469

Interaction is exothermic and may be violent.

Non-metals

Mellor, 1963, Vol. 2, Suppl. 2.2, 2174—2175

The molten metal ignites in sulfur vapour, and reacts with various forms of carbon exothermically, one product, the interstitial rubidium octacarbide, being pyrophoric.

Vanadium trichloride oxide

Mellor, 1963, Vol. 2, Suppl. 2.2, 2176

Interaction is violent at 60°C.

Water

1. Mellor, 1941, Vol. 2, 469
2. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633—636

Contact with cold water is exothermic enough to ignite the hydrogen evolved [1]. Reactivity of rubidium and other alkali metals with water has been discussed in detail [2].

See ALKALI METALS, PYROPHORIC METALS

See other METALS

4884. Rhenium

[7440-15-5] **Re**

Re

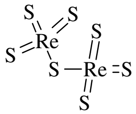
Oxygen (Gas)

See Oxygen (Gas): Rhenium

See other METALS

4885. Rhenium(VII) sulfide

[12038-67-4] **Re_2S_7**



Sidgwick, 1950, 1299

It is readily oxidised in air, sometimes igniting.

See other METAL SULFIDES

4886. Rhodium

[7440-16-6] **Rh**

Rh

Sidgwick, 1950, 1513
Metallic rhodium prepared by heating its compounds in hydrogen must be allowed to cool in an inert atmosphere to prevent catalytic ignition of the sorbed hydrogen on exposure to air.
See Zinc: Catalytic metals

Interhalogens
See Chlorine trifluoride: Metals
Bromine pentafluoride: Acids, etc.
See other HYDROGENATION CATALYSTS, METALS, PYROPHORIC METALS

4887. Radon
[10043-92-2] **Rn**

Rn

Water
John, G., *Health Phys.*, 1985, **49**, 977—979
A 22 year old glass ampoule containing an aqueous solution of radon was under considerable pressure when opened and ejected the top vigorously. This was attributed to formation of hydrogen by radiolysis of the solvent water.
See Americium trichloride
See other IRRADIATION DECOMPOSITION INCIDENTS

4888. Ruthenium
[7440-18-8] **Ru**

Ru

1. Mellor, 1942, Vol. 15, 502
2. Ullmann, 1992, Vol. A21, 125/6

Dissolution of a zinc—ruthenium alloy in hydrochloric acid leaves an explosive residue of finely divided ruthenium [1]. More probably this is the hydride, which may decompose on slight stimulus, the evolved hydrogen probably igniting because of the catalytic activity of the metal. Ruthenium prepared from its compounds by borohydride reduction is especially dangerous in this respect [2].

Aqua regia, Potassium chlorate
See Potassium chlorate: Aqua regia, etc.
See other HYDROGENATION CATALYSTS, METALS

4889. Ruthenium(IV) sulfide
[12166-20-0] **RuS_2**

S=Ru=S

Air, or Carbon dioxide
Mellor, 1942, Vol. 15, 541

The sulfide decomposes explosively if heated in air or air—nitrogen mixtures, and incandesces, then explodes if heated under carbon dioxide.
See other METAL SULFIDES

4890. Ruthenium salts

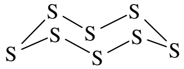
[22541-59-9] (2+) [22541-88-4] (3+) **RuZ_2**
RuZ_3

Ru^{2+} Ru^{3+}

Sodium tetrahydroborate
See Sodium tetrahydroborate: Ruthenium salts

†4891. Sulfur

[7704-34-9] **S**



(*MCA SD-74*, 1959); *NSC 612*, 1979 (solid); *NSC 592*, 1978 (liquid); *FPA H14*, 1973; *HCS 1980*, 871 (liquid), 872 (solid)
NFPA 655, Quincy (Ma), Natl. Fire Prot. Assoc., 1988

1. *MCA SD-74*, 1959
2. Anon., *Loss Prev. Bull.*, 1987, (078), 23—25
3. Ayers, P. G., *Loss. Prev. Bull.*, 1988, (094), 34
4. Poole, G. A., *Loss. Prev. Bull.*, 1988, (084), 35

The new US National Fire Code covers the precautions necessary to prevent fires or explosions during crushing of the solid, or during handling of the molten element.

It may become ignited through frictional heat or incendive sparks, particularly when suspended as dust in air, for which the approximate explosive limits are 35—1400 g/m^3. Handling precautions for the solid and molten element are detailed. In the hazardous reactions listed below, the dual capacity of sulfur to oxidise or be oxidised is apparent [1]. Molten sulfur at '150—200°C' was being transported in a truck with two tank trailers each holding 12 t (57% of capacity). A traffic accident on a bridge caused both tanks to vault over the central barrier (thought to be caused by surging of the tank contents), and the impact caused tank rupture and ignition of the spilled hot sulfur. The fire led to dense clouds of sulfur dioxide and smoke which greatly hampered emergency services. The flash point of pure sulfur is 188°C, but impure sulfur may ignite at 168°C [2]. Later correspondents corrected the temperature limits for transportation of molten sulfur to 130—140° or 132—149°C [3,4]. Several values have been quoted in the literature for both flash point and autoignition temperature of molten sulfur, e.g. fl.p. 168, 188; a.i.t. 190, 232°C.
See entry HIGH SURFACE-AREA SOLIDS

Aluminium, Copper
See Aluminium: Copper, Sulfur

Aluminium, Starch
Biasutti, 1981, 138
Ignition of a dry mixture of the 3 powdered materials being mixed in a screw extruder led to a minor explosion, then a major dust explosion.

Calcium, Vanadium pentaoxide
See Vanadium(V) oxide: Calcium, etc.

Diethyl ether
Taylor, H. F., *J. R. Inst. Chem.*, 1955, **79**, 43
Evaporation of an ethereal extract of sulfur caused an explosion of great violence. Experiment showed that evaporation of wet, peroxidised ether gave a mildly explosive residue, which became violently explosive on addition of sulfur.

Fibreglass, Iron
Anon., *Info. Circ. No. 8272(10)*, Washington, US Bur. Mines, 1964
A mixture of sulfur with iron filings and fibreglass reacts exothermally at 125—145°C.
See Metals, below (reference 12)

Fluorine
See Fluorine: Non-metals

Halogen oxides MRH Chlorine dioxide 4.64/76, chlorine trioxide 7.57/60, dichlorine oxide 3.01/89, trioxygen difluoride 6.82/67
Mellor, 1941, Vol. 2, 289, 241, 295; 1956, Vol. 2, Suppl. 1, 540, 542
Sulfur ignites in chlorine dioxide gas, and may cause an explosion, which usually happens on contact of sulfur with the very unstable dichlorine monoxide. Iodine(V) oxide reacts explosively on warming with sulfur. Chlorine trioxide would be expected to oxidise sulfur violently but dichlorine heptaoxide does not react.
See ‘Trioxygen difluoride’: Various materials

Interhalogens
See Bromine pentafluoride: Acids, etc.
See Bromine trifluoride: Halogens, etc.
See Chlorine trifluoride: Metals, etc. MRH 4.10/85
See Iodine pentafluoride: Metals, etc.

Limonene
Nolan, 1983, Case history 216
Addition of molten sulfur to limonene in a 9 kl reactor led to a violent runaway exothermic reaction. Small scale pilot runs had not shown the possibility of this. Heating terpenes strongly with sulfur usually leads to formation of benzene derivatives with evolution of hydrogen sulfide.
See other GAS EVOLUTION INCIDENTS

Metal acetylides or carbides

Mellor, 1946, Vol. 5, 849, 862, 886, 891

Monorubidium acetylide ignites in molten sulfur; barium carbide ignites in sulfur vapour at 150°C and incandesces; while calcium, strontium, barium and uranium carbides need a temperature around 500°C to ignite.

Metal halogenates

See METAL HALOGENATES: Non-metals
See also METAL CHLORATES: Phosphorus, etc.

Metal oxides — MRH values show % of oxide

See Lead(IV) oxide: Non-metals
'Mercury(I) oxide': Non-metals
Mercury(II) oxide: Non-metals
Silver(I) oxide: Non-metals
Sodium peroxide: Non-metals — MRH 3.35/71
Thallium(III) oxide: Sulfur
Chromium trioxide: Sulfur — MRH 1.76/86

Metals — MRH Aluminium 4.81/36, calcium 6.69/56, magnesium 6.15/43, rubidium 1.76/84, sodium 4.81/59, zinc 2.09/67

1. Mellor, 1940, Vol. 4, 268, 480
2. Mellor, 1941, Vol. 3, 639
3. Mellor, 1946, Vol. 5, 210, 393
4. Mellor, 1942, Vol. 15, 149, 527, 627, 696
5. Mellor, 1941, Vol. 7, 208, 328
6. Mellor, 1942, Vol. 12, 31
7. Rothman, R., *Philad. Astronaut. Soc. Bull.*, 1953, **1**, 7
8. Sleight, A. W. *et al., Inorg. Synth.*, 1973, **14**, 152—153
9. Revelli, J. F., *Inorg. Synth.*, 1979, **19**, 35
10. Kotoyori, T. *et al., Chem. Abs.*, 1984, **100**, 197111
11. Partington, 1946, 552—853
12. Ephraim, 1939, 519
13. Chakurov, Kh. *et al., J. Solid State Chem.*, 1987, **71**, 522—529

A mixture of sulfur with powdered zinc explodes on warming, and that with cadmium reacts rather less vigorously [1]. Mixtures of calcium and sulfur explode on ignition and calcium burns in sulfur vapour at 400°C [2]. Indium [3], palladium and rhodium [4], thorium and tin [5] all ignite and incandesce on heating admixed with sulfur. Uranium [6], osmium and nickel [4] (powders) ignite and incandesce in boiling sulfur or its vapours at 600°C, although more finely divided (catalytic) forms of nickel should react more readily. Magnesium will react when red-hot or molten, with molten sulfur or its vapour [1] and a mixture of aluminium powder and sulfur will burn violently or explode if ignited with a high temperature (magnesium) fuse [3]. Intimate mixtures of micro-grained zinc and sulfur were used as a rocket propellant [7]. In the reaction of gadolinium and sulfur in a heated quartz ampoule to prepare gadolinium sulfide, good temperature control is necessary to prevent violent interaction, with attack and possible rupture of the ampoule [8]. The same is true of the reaction of tantalum with sulfur [9]. Spontaneous combustion occurred in a copper powder—sulfur mixture used in manufacture of brake pads. Thermal analysis showed that the mixture ignited at 115°C. Preventive measures are discussed [10]. Iron filings burn when sprinkled into sulfur vapour, and a mixture with powdered sulfur attains incandescence when heated. Addition of water to the dry mixture will initiate an exothermic reaction [11]. Mercury, iron, magnesium or copper will react exothermally with sulfur at ambient temperature if the state of subdivision is fine enough [12]. In the preparation of the sulfides of cadmium, tin and zinc by 'mechanochemical reaction' (grinding?), the violent, often explosive reactions can be rendered non-explosive by the presence of a critical amount of inert material, and a mechanism is proposed [13].

See Lithium: Sulfur
  Potassium: Sulfur
  Rubidium: Non-metals
  Sodium: Non-metals
  Aluminium, Copper, above
See Selenium: Metals
See also Aluminium, Starch, above
See also Fibreglass, Iron, above

Non-metals

1. Mellor, 1946, Vol. 5, 15
2. von Schwartz, 1918, 328
3. Mellor, 1940, Vol. 8. 786
4. Phillips, R., *Org. Synth.*, 1943, Coll. Vol. 2, 579

Boron reacts with sulfur at 600°C becoming incandescent [1]. Mixtures of sulfur with lamp black or freshly calcined charcoal ignite spontaneously, probably owing to adsorbed oxygen on the catalytic surface [2]. Mixtures of yellow phosphorus and sulfur ignite and/or explode on heating [3]. Ignition of an intimate mixture of red phosphorus and sulfur causes a violent exothermic reaction [4].

Other reactants

Yoshida, 1980, 37—38

MRH values calculated for 32 combinations, mainly with oxidants, are given.

Oxidants — MRH values show % of oxidant

1. Ivanov, V. G. *et al., Chem. Abs.*, 1980, **93**, 116708
2. Ivanov, V. G. *et al., Chem. Abs.*, 1981, **94**, 86592

The self-ignition of sulfur with potassium chlorate or iodine(V) oxide at 145—160°C, and with potassium perchlorate at 385°C was studied using DTA [1], and combustion characterisitics of the mixtures were determined [2].

See Halogen oxides, Interhalogens, Metal oxides, all above
  Ammonium nitrate: Sulfur — MRH 3.01/88
  Barium bromate: Sulfur — MRH 2.26/88
  Chromyl chloride: Non-metals
  Fluorine: Non-metals — MRH 8.28/78

Heptasilver nitrate octaoxide: Alone, or Sulfides, etc.	
Lead chromate: Sulfur	
Lead(II) chlorite: Non-metals	
Phosphorus(III) oxide	
Potassium bromate: Non-metals	MRH 2.55/86
Potassium chlorate: Charcoal, etc., or: Non-metals	MRH 3.22/82
Potassium chlorite: Sulfur	
Potassium perchlorate: Sulfur	MRH 3.39/79
Potassium permanganate: Non-metals	MRH 1.63/90
Silver bromate: Sulfur compounds	MRH 2.00/88
Silver chlorite: Hydrochloric acid, etc.	
Silver nitrate: Non-metals	MRH 1.67/84
Sodium chlorate: Ammonium salts, etc.	MRH 4.27/80
Tetraphosphorus hexaoxide: Sulfur	

Potassium nitride
Mellor, 1940, Vol. 8, 99
Potassium nitride and other alkali metal nitrides react with sulfur to form a highly flammable mixture, which evolves ammonia and hydrogen sulfide in contact with water.
See Caesium nitride

Sodium hydride
Mellor, 1941, Vol. 2, 483
Interaction with sulfur vapour is vigorous.

Static discharges
Enstad, G., *A Reconsideration of the Concept of Minimum Ignition Energy*, paper at Euro. Fed. Chem. Engrs. Wkg. Party meeting, 16th March, 1975.
Sulfur dust has a very low minimum ignition energy (3 mJ), so particular care is necessary in formulating protective measures.

Tetraphenyllead
See Tetraphenyllead: Sulfur
See other NON-METALS, OXIDANTS

4892. Silicon monosulfide

[12504-41-5] **SSi**

$$Si{=}S$$

Water
Bailar, 1973, Vol. 1, 1355
It reacts rapidly with water and may ignite.
See other NON-METAL SULFIDES

4893. Samarium sulfide

[29678-92-0] **SSm**

$\mathrm{Sm{=}S}$

Gadolinium sulfide

Jayaraman, A. *et al., Phys. Rev. Lett.*, 1973, **31**, 700

Cooling of samples of crystalline samarium sulfide containing 22 atom% of gadolinium in the lattice to below —153°C causes a near-explosive rearrangement to a powder form. This was attributed to changes in the lattice constants corresponding to a volume increase of 7.5%.

See other METAL SULFIDES

4894. Tin(II) sulfide

[1314-95-0] **SSn**

$\mathrm{Sn{=}S}$

See entry REFRACTORY POWDERS

Oxidants

Dichlorine oxide: Oxidisable materials

See Chloric acid: Metal sulfides

See also METAL HALOGENATES: Metals, etc.

See other METAL SULFIDES

4895. Strontium sulfide

[1314-96-1] **SSr**

$\mathrm{Sr{=}S}$

Lead dioxide

See Lead(IV) oxide: Metal sulfides

See other METAL SULFIDES

4896. Tin(IV) sulfide

[1315-01-1] **S_2Sn**

$\mathrm{S{=}Sn{=}S}$

Oxidants

Dichlorine oxide: Oxidisable materials

See Chloric acid: Metal sulfides

See METAL HALOGENATES: Metals, etc.

See other METAL SULFIDES

4897. Tantalum(IV) sulfide

[12143-72-5] **S_2Ta**

$S{=}Ta{=}S$

Preparative hazard

See Sulfur: Metals (reference 9)

See other METAL SULFIDES

4898. Titanium(IV) sulfide

[12039-13-3] **S_2Ti**

$S{=}Ti{=}S$

Potassium nitrate

See Potassium nitrate: Metal sulfides

See other METAL SULFIDES

4899. Uranium(IV) sulfide

[12039-14-4] **S_2U**

$S{=}U{=}S$

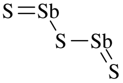
Nitric acid

See Nitric acid: Uranium disulfide

See other METAL SULFIDES

4900. Antimony trisulfide

[1345-04-6] **S_3Sb_2**



Other reactants

Yoshida, 1980, 130

MRH values calculated for 11 combinations with various materials are given.

Oxidants MRH values show % of oxidant.

See Chloric acid: Metal sulfides
  Dichlorine oxide: Oxidisable materials MRH 3.72/49
  Fluorine: Sulfides MRH 6.40/56
  Heptasilver nitrate octaoxide: Alone, or Sulfides
  Lead(II) chlorite: Antimony sulfide
  Potassium chlorate: Metal sulfides MRH 2.84/61
  Potassium nitrate: Metal sulfides MRH 2.30/63
  Silver(I) oxide: Metal sulfides
  Thallium(III) oxide: Sulfur, etc.

See other METAL SULFIDES

4901. Antimony
[7440-36-0] **Sb**

Sb

NSC 408, 1978 (metal and compounds)

Krebs, H. *et al., Z. Anorg. Chem.*, 1955, **282**, 177
Electrolysis of acidified, stirred antimony halide solutions at low current density produces explosive antimony which contains substantial amounts of halogen.

Alkali nitrates
Mellor, 1947, Vol. 9, 382
Mixtures detonate on heating, forming antimonates.

Aluminium
See Aluminium: Antimony, etc.

Disulfur dibromide
See Disulfur dibromide: Metals

Halogens — MRH Chlorine 1.67/47, fluorine 5.10/32
Mellor, 1947, Vol. 9, 379
Antimony ignites in fluorine, chlorine and bromine. With iodine, ignition or explosion may occur if quantities are large enough.

Other reactants
Yoshida, 1980, 34
MRH values calculated for 9 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Ammonium nitrate: Metals	MRH 2.30/62
Bromine pentafluoride: Acids, etc.	MRH 2.76/46
Bromine trifluoride: Halogens, etc.	MRH 2.34/53
Chloric acid: Metals, etc.	
Chlorine trifluoride: Metals, etc.	MRH 3.47/36
Dichlorine oxide: Oxidisable materials	MRH 2.64/41
Halogens, above	
Iodine pentafluoride: Metals	
Iodine: Metals	
Nitrosyl fluoride: Metals	
Perchloric acid: Antimony(III) compounds	
Potassium dioxide: Metals	
Potassium permanganate: Antimony, etc.	MRH 0.25/86
Seleninyl chloride: Antimony	
Sodium nitrate: Antimony	

See other METALS

4902. Selenium
[7782-49-2] **Se**

Se

NSC 578, 1982 (element and compounds)

Hexalithium disilicide
See Hexalithium disilicide: Non-metals

Metal acetylides or carbides
Mellor, 1946, Vol. 5, 862, 886
Metal acetylides incandesce on heating in selenium vapour; barium acetylide at 150°C, calcium acetylide and strontium acetylide at 500°C; and thorium carbide at an unstated temperature.
See Rubidium acetylide: Non-metals

Metal amides
Pascal, 1960, Vol. 16.2, 1724
Interaction of selenium with alkali metal amides and alkaline earth metal amides gives explosive products.

Metal chlorates
Mellor, 1956, Vol. 2, Suppl. 1, 583
A slightly moist mixture of selenium with any chlorate (except of alkali metals) becomes incandescent.
See METAL HALOGENATES: Non-metals

Metals

1. Mellor, 1942, Vol. 15, 151
2. Mellor, 1947, Vol. 10, 766—777
3. Mellor, 1942, Vol. 12, 31
4. Mellor, 1940, Vol. 4, 480
5. Mellor, 1942, Vol. 16, 158
6. Reisman, A. *et al., J. Phys. Chem.*, 1963, **67**, 22
7. Bailar, 1973, Vol. 2, 79

Nickel and selenium interact with incandescence on gentle heating [1], as do also sodium and potassium, the latter mildly explosively [2]. Uranium [3] and zinc [4] also incandesce when their mixtures with selenium are heated, and platinum sponge incandesces vividly [5]. The particle size of cadmium and selenium must be below a critical size to prevent explosions during synthesis of cadmium selenide by heating the elements together. Similar considerations also apply to interaction of cadmium or zinc with sulfur, selenium or tellurium [6]. Interaction of powdered tin and selenium at 350°C is extremely exothermic [7].

Nitrogen trichloride
See Nitrogen trichloride: Initiators

Oxidants

See Barium peroxide: Selenium
  Bromine pentafluoride: Acids, etc.
  Chlorine trifluoride: Metals, etc.
  Chromium trioxide: Selenium
  Fluorine: Non-metals
  Metal chlorates, above; Oxygen, etc., below
  Potassium bromate: Non-metals
  Silver(I) oxide: Non-metals
  Sodium peroxide: Non-metals

Oxygen, Organic matter

1. Astin, S. *et al., J. Chem. Soc.*, 1933, 391
2. Watkins, C. R. *et al., Chem. Rev.*, 1945, **36**, 235

During attempted conversion of recovered selenium metal to the dioxide by heating in oxygen, a vigorous explosion occurred. This was attributed to selenium-catalysed oxidation of traces of organic impurities in the selenium. Oxidation of recovered selenium with nitric acid is rendered vigorous by presence of organic impurities, but is a safe procedure [1]. The later reference incorrectly attributed the explosions to the nitric acid procedure [2].

Phosphorus

Pascal, 1956, Vol. 10, 724

Interaction warm attains incandescence.

See related METALS, NON-METALS

4903. Silicon

[7440-21-3] **Si**

Si

1. Eckhoff, R. K. *et al., J. Electrochem. Soc.*, 1986, **133**, 2631—2637
2. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
3. See entry Silane (reference 4)
4. Tamme, G. *et al., Chem. Abs.*, 2000, **133**, 197587r
5. Clement, D. *et al., Chem. Abs.* 2004, **141**, 381716y

Finely powdered silicon can give significant dust explosion hazards. Relationships of sensitivity to spark ignition and of explosibility to particle size are studied [1]. Maximum explosion pressures of 6.4 bar, with maximum rate of rise of 884 bar/s have been determined [2]. Silicon dust is likely to result from processes using silanes in the gas phase [3]. There is a suggestion that silicon dust may react hazardously with metal oxides (thermite reaction), alkyl halides and nitrogen. The reaction between the dust and copper oxide is a processing danger [4]. [Other thermite reactions of silicon

are known and sometimes exploited]. Porous silicon wafers, the pores filled with oxidants, are suggested as explosives [5].
See other THERMITE REACTIONS

Calcium
See Calcium: Silicon

Metal acetylides
See Rubidium acetylide: Non-metals
Caesium acetylide: Non-metals

Metal carbonates
Mellor, 1940, Vol. 6, 164
Amorphous or crystalline silicon both react exothermally when heated with alkali-metal carbonates, attaining incandescence and evolving carbon monoxide.

Metal hexafluorides
1. Paine, R. T. *et al., Inorg. Chem.*, 1975, **14**, 1111
2. Paine, R. T. *et al., Inorg. Synth.*, 1979, **19**, 138

During the reduction of iridium hexafluoride, osmium hexafluoride or rhenium hexafluoride with silicon to the pentafluorides, the hexafluorides must not be condensed directly onto undiluted silicon powder, or explosions may result [1]. The same is true for molybdenum hexafluoride and uranium hexafluoride [2].

Metal oxides
Tamme, G. *et al., Chem. Abs.*, 2000, **133**, 197587r
It is suggested that the thermite reaction betwen silicon dust and copper oxide (the abstract does not state which) is a potential processing danger. Other thermite reactions of silicon are known and sometimes used.
See other THERMITE REACTIONS

Oxidants
See Bromine trifluoride: Halogens, etc.
Chlorine trifluoride: Metals, etc.
Chlorine: Non-metals
Cobalt trifluoride: Silicon
Fluorine: Non-metals
Iodine pentafluoride: Metals, etc.
Lead(II) oxide: Non-metals
Metal hexafluorides, above
Nitrosyl fluoride: Metals, etc.
Oxygen difluoride: Non-metals
Peroxyformic acid: Non-metals
Silver fluoride: Non-metals

Water
See Boron: Water
See related METALS, NON-METALS

4904. Silicon—zirconium alloys

[12138-26-0] (1:1) [12211-03-9] (1:2) **Si—Zr**

Si—Zr

See Zirconium (reference 6)
See other ALLOYS

4905. Samarium

[7440-31-5] **Sm**

Sm

1,1,2-Trichlorotrifluoroethane
Anon., *NSC Newsletter, R & D Sect.*, 1970, (8)
An attempt to mill a slurry of metal in the solvent caused a violent explosion. Experiment showed violent interaction of the freshly ground metal surfaces with the halocarbon solvent.
See other METAL—HALOCARBON INCIDENTS, METALS

4906. Tin

[7440-31-5] **Sn**

Sn

HCS 1980, 901 (powder)

Carbon tetrachloride, Water
Pascal, 1963, Vol. 8.3, 309
In the presence of water vapour, interaction is violent
See other METAL—HALOCARBON INCIDENTS

Disulfur dichloride
See Disulfur dichloride: Tin

Other reactants
Yoshida, 1980, 217
MRH Values calculated for 9 combinations with oxidants are given.

Oxidants	MRH values show % of oxidant
See Ammonium nitrate: Metals	MRH 2.92/58
Chlorine trifluoride: Metals	
Chlorine: Metals	MRH 2.09/55
Copper(II) nitrate: Tin	MRH 2.68/38
Fluorine: Metals	
Iodine bromide: Metals	
Iodine heptafluoride: Metals	

Potassium dioxide: Metals
Sodium peroxide: Metals — MRH 1.38/56
Sulfur: Metals
Tellurium: Tin

Water

1. Board, S. J. *et al., Int. J. Heat Mass Transf.*, 1974, **17**, 331—339
2. Board, S. J. *et al., Chem. Abs.*, 1975, **83**, 12950
3. Frost, D. L. *et al., Progr. Astronaut. Aeronaut.*, 1988, **114** (Dynam. Explos.), 451—473

Experiments involving explosions of molten tin and water are described [1], and the mechanism of propagation of the thermal explosions was studied [2]. The dynamics of explosive interaction between multiple drops of molten tin and water has been examined experimentally [3].

See MOLTEN METAL EXPLOSIONS

See other METALS

4907. Strontium

[7440-25-7] **Sr**

Sr

Sorbe, 1968, 154

The finely divided metal may ignite in air.

Halogens

Pascal, 1958, Vol. 4, 579

At 300°C strontium incandesces in chlorine, and at 400°C it ignites in bromine vapour.

Water

Pascal, 1958, Vol. 4, 579

Interaction is more vigorous than with calcium.

See other METALS, PYROPHORIC METALS

4908. Tantalum

[7440-25-7] **Ta**

Ta

1. Izumi, T., *Chem. Abs.*, 1999, **131**, 341149c
2. Matsuda, T. *et al., J. Haz. Mat.*, 2000, **77**(1-3), 33

Although very unreactive in massive forms, the finely divided metal may be pyrophoric, a Japanese study of this hazard has been reported [1]. Consequent upon an explosion in a tantalum dust collector, further study of powder explosion was made. Minimum ignition energies were found to be much lower than previously supposed. An oxide coating makes it susceptible to electrostatic charge generaton and discharge [2].

See entry PYROPHORIC METALS (references 3,9)

Bromine trifluoride
See Bromine trifluoride: Halogens, etc.

Fluorine
See Fluorine: Metals

Lead chromate
See Lead chromate: Tantalum
See other METALS

4909. Technetium
[7440-26-8] **Tc**

Tc

Bailar, 1973, Vol. 3, 881
In finely divided forms (sponge or powder) it readily burns in air to the heptaoxide.
See other METALS, PYROPHORIC METALS

4910. Tellurium
[13494-80-9] **Te**

Te

Halogens, or Interhalogens
See Bromine pentafluoride: Acids, etc.
Chlorine fluoride: Tellurium
Chlorine trifluoride: Metals
Chlorine: Non-metals
Fluorine: Non-metals

Hexalithium disilcide
See Hexalithium disilicide: Non-metals

Metals
See Cadmium: Selenium, etc.
Platinum: Selenium, etc.
Potassium: Selenium, etc.
Sodium: Non-metals

Silver iodate
See Silver iodate: Tellurium

Tin
Bailar, 1973, Vol. 2, 80
Interaction hot to give tin telluride attains incandescence.
See Selenium: Metals
See related METALS, NON-METALS

4911. Thorium

[7440-29-1] **Th**

Th

1. Mellor, 1941, Vol. 7, 207
2. Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64
3. *Fire Record Bull. FR58-3*, Boston, NFPA, 1958

The massive metal ignites below red-heat when heated in air, and the powdered metal ignites when rubbed or crushed [1], or on pouring as a stream in air, owing to intergranular friction. Storage and handling precautions are discussed [2]. During destruction by burning of radioactive thorium scrap, addition of a 4 cm lump of the metal waste to burning thorium wafers led to a series of violent explosions. This was attributed to presence of water or other impurities in the lump [3].

See THORIUM FURNACE RESIDUES

Carbon dioxide, Nitrogen
See Carbon dioxide: Metals, Nitrogen

Halogens
Mellor, 1941, Vol. 7, 207
Thorium incandesces in chlorine, bromine or iodine, and would be expected to ignite readily in fluorine.

Nitryl fluoride
See Nitryl fluoride: Metals

Oxygen
Mellor, 1941, Vol. 7, 207
The massive metal ignites on heating in oxygen.

Peroxyformic acid
See Peroxyformic acid: Metals

Phosphorus
See Phosphorus: Metals

Silver
See Silver—thorium alloy

Sulfur
See Sulfur: Metals
See other METALS, PYROPHORIC METALS

4912. Thorium salts

[16065-92-2] **Th^{4+}**

Th^{4+}

'Cupferron'
See Ammonium *N*-Nitrosophenylaminooxide: Thorium salts

4913. Titanium
[7440-32-6] **Ti**

Ti

NSC 485, 1968; *FPA H87*, 1980

1. Mellor, 1941, Vol. 7, 19
2. Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64
3. *NSC Data Sheet 485*, 1968
4. Lowry, R. N. *et al., Inorg. Synth.*, 1967, **10**, 3
5. *Standard for Production, Processing, Handling and Storage of Titanium*, NFPA 481, Quincy (Ma), 1987
6. Alekseev, A. G. *et al., Chem. Abs.*, 1975, **83**, 83527
7. Popov, E. I. *et al., Chem. Abs.*, 1975, **83**, 150922
8. Elrod, C. W., *Chem. Abs.*, 1982, **97**, 184846
9. Poyarkov, V. G. *et al., Chem. Abs.*, 1983, **98**, 37077
10. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
11. Prine, B. A., *Plant/Oper. Progr.*, 1992, **11**(2), 113
12. Mahnken, G. E. *et al., Process Safety Progress*, 1997, **16**(1), 54
13. Mahnken, G., *Chem. Eng. Progr.*, 2000, **96**(4), 47
14. Mary Kay O'Connor Process Safety Centre, Safety Alert, 03 Aug, 2001

While massive titanium ignites in air only at 1200°C [1], the finely divided metal is very pyrophoric and should be stored damp in metal containers [2]. Titanium fires are difficult to extinguish as it burns brilliantly in nitrogen above 800°C, in carbon dioxide above 550°C [3], and may react explosively with metal carbonates [1]. Residual titanium sponge after vapour phase reaction with iodine at 400—425°C is often pyrophoric [4]. All aspects of preventing hazards in use of titanium are covered in a US Standard [5]. Powdered metal made by calcium hydride reduction shows a greater explosion hazard than electrolytically reduced metal. The effect of inert gases was also examined [6]. The relationship between spontaneous ignition temperatures (250—600°C) and lower explosive limits (40—300 mg/l) of titanium powders was studied [7]. Incidents involving combustion of titanium components in aviation gas turbines are reviewed [8]. Ignition parameters for titanium powder of < 100 μ particle size were determined. Ignition temperature decreases from 640 to 508°C with increase in specific surface area from 960 to 1520 cm^2/g [9]. Maximum explosion pressures of 5.8 bar, with maximum rates of rise of 816 bar/s have been determined [10]. Titanium combustion as a result of welding operations appears to be potentiated by carbon steel, there are several recorded cases, mechanism not established [11]. Another fire when cutting into a steel-clad Ti heat-exchanger, with explosions when sprayed with water, is reported [12]. A review of such incidents suggests that the effect of steel could be titanium ignition through a thermite reaction with hot steel slag [13]. Limited evidence has been obtained for such reaction after another fire, started by a grinder, in titanium column packing coated by what looked like rust particles [14].

Aluminium

See Aluminium—titanium alloys

Bromine trifluoride

See Bromine trifluoride: Halogens, etc.

Carbon black

Afanas'eva, L. F. *et al., Chem. Abs.*, 1981, **95**, 64482

Fire hazards and pyrophoricity of mixed charges for preparing titanium carbide are discussed.

Carbon dioxide, Nitrogen

See Carbon dioxide: Metals, or: Metals, Nitrogen

Carbon dioxide, or Metal carbonates

1. Stout, E. L., *Chem. Eng. News*, 1958, **36**(8), 64
2. Mellor, 1941, Vol. 7, 20

Titanium powder has ignited as a thin layer under carbon dioxide, and burns in the gas above 550°C [1]. Contact of titanium with fused alkali-metal carbonates causes incandescence [2].

Halocarbons

Pot. Incid. Rep. 39, ASESB, Washington, 1968

Mixtures of powdered titanium and trichloroethylene or 1,1,2-trichlorotrifluoroethane flash or spark under heavy impact.

See other METAL—HALOCARBON INCIDENTS

Halogens

1. Mellor, 1941, Vol. 7, 192
2. Kirk-Othmer, 1969, Vol. 20, 372
3. Denes, G., *Chem. Eng. News*, 1987, **65**(7), 2
4. Fast, J. D., *Rec. Trav. Chim.*, 1939, **58**, 174
5. Cobb, C. M., *Chem. Eng. News*, 1987, **65**(14), 2
6. Sisler, H. H., *Chem. Abs.*, 1988, **108**, 15143
7. Asrar, N. *et al., Materials Performance*, 2000, **39**(10), 62

Reaction of heated titanium with the halogens usually causes ignition and incandescence (chlorine at 350°C, bromine at 360°C, iodine higher, but weak combustion) [1], especially in absence of moisture [2]. Attempts to prepare titanium tetraiodide (5 g) by heating titanium powder with iodine in sealed copper tubes heated in a water bath led to explosions when the bath temperature reached 90°C. Rupture of the tubes also occurred with 0.5 g preparations [3]. Attempts to prepare titanium diiodide according to an earlier high-vacuum procedure [4] also led to violent explosions after two days [5]. A procedure to prepare the tetraiodide by heating a mixture of titanium and excess iodine in a Pyrex glass apparatus is reported [6]. Spontaneous ignition of titanium instrumentation in damp chlorine at somewhat below ambient temperature occurred and was investigated [7].

See Chlorine: Metals (references 2,3)

See also Fluorine: Metals

See other HALOGENATION INCIDENTS

Metal oxides MRH Chromium trioxide 4.85/73

Mellor, 1961, Vol. 7, 20

Interaction with copper(II) oxide or lead(II,IV) oxide is violent.

Metal oxosalts

Mellor, 1941, Vol. 7, 20

Contact of powdered titanium with molten potassium chlorate, alkali-metal carbonates or mixed potassium carbonate/nitrate causes vivid incandescence.

Nitric acid MRH 8.79/51

1. Anon., *Occ. Health and Safety*, 1957, **7**, 214
2. Anon., *Chem. Eng. News*, 1953, **31**, 3320

Investigation showed that commercial titanium alloys in contact with acid containing less than 1.34% water and more than 6% of dinitrogen tetraoxide may become sensitive to impact, and react explosively with the acid. Possible causes are discussed [1]. The spongy residue formed by prolonged corrosion of titanium—manganese alloys by red fuming nitric acid will explode on exposure to friction or heat [2].

See other CORROSION INCIDENTS

Nitrogen

Bailar, 1973, Vol. 3, 359

Titanium is claimed to be the only element that will burn in nitrogen.

See Lithium, Nitrogen: Magnesium

Nitryl fluoride

See Nitryl fluoride: Metals

Other reactants

Yoshida, 1980, 231

MRH values for 13 combinations with oxidants are given.

Oxidants

MRH Ammonium nitrate 5.48/77, hydrogen peroxide 8.74/59, potassium permanganate 3.97/63, sodium bromate 6.19/68, sodium chlorate 8.45/60, sodium chlorite 7.36/65, sodium nitrate 6.07/58, sodium perchlorate 8.37/57, sodium peroxide 3.51/76

Mellor, 1941, Vol. 7, 20

Mixtures of the powdered metal with potassium chlorate, potassium nitrate or potassium permanganate react explosively on heating. Addition of the powdered metal to fused potassium chlorate at 370°C leads to incandescence.

See Iodine: Metals

See Metal oxides; Nitric acid, both above

See Potassium perchlorate: Metal powders (references 1,3)

See Sodium chlorate, below

Oxygen

1. Kirk-Othmer, 1969, Vol. 20, 372
2. Komamiya, K., *Chem. Abs.*, 1982, **96**, 90906
3. Shenoy, V. R., *Chem. Eng. News*, 1992, **70**(40), 4
4. Anon., *Sichere Chemiearbeit*, 1994, **46**(6), 67

Ignition may occur in liquid or gaseous oxygen and in gas mixtures containing over 46% oxygen, under impact or abrasion. Mixtures of powdered titanium and liquid oxygen are detonable [1]. In the absence of a surface film of grease, etc. on a freshly abraded surface, titanium will not burn under high pressure oxygen at high temperature [2]. Two explosions were experienced when studying treatment of ppm levels of organics in waste under 3-4 bar of oxygen at around 200°C. In each case the problem seems to have started at joints where abrasion, flakes of metal, grease and/or polymeric seals might have been present [3]. An inaccessible valve of partly titanium construction in a line filled with oxygen at 140°C (pressure unspecified) ignited for no apparent reason and burnt out. Titanium is not a suitable material of construction for oxygen lines, being even less protected by its oxide coating than is aluminium [4].
See Oxygen (Gas): Titanium
See also Oxygen (Gas): Polytetrafluoroethylene, Stainless steel
See also Oxygen (Liquid): Metals

Platinum group metals
Ullmann, 1992, Vol. A21, 125/6
Alloy formation between the powdered metals may be violent

Silver fluoride
See Silver fluoride: Titanium

Silver nitrate
See Silver nitrate: titanium

Sodium chlorate, Water MRH 8.45/60
Scribner, H. C., *Tappi J.*, 1986, **69**(12), 16
A steam-heated titanum heat exchanger was used to heat sodium chlorate solution passing through its tubes, some of which were blocked by polypropylene film and wood chip debris. This led to local boiling and separation of solid sodium chlorate, which ignited the organic material and heated the titanium tube to its ignition point (427°C). It then started to burn, reacting with steam to liberate hydrogen which led to a violent explosion.
See other GAS EVOLUTION INCIDENTS

Water

1. Mellor, 1941, Vol. 7, 19
2. Anon., *Loss Prev. Bull.*, 1987, (075), 22
3. Sabo, A., The Oregonian, 1999, Oct. 1st

Finely divided titanium reacts with steam at 700°C, and in presence of air the evolved hydrogen may ignite or explode [1]. A heat exchanger with titanium tubes was being dismantled with flame cutting equipment, which caused ignition of the hot titanium in air. Application of water to extinguish the violent fire led to evolution of hydrogen and then an explosion [2]. An explosion occurred when casting titanium in a water-cooled copper crucible. An outlet valve for the water was closed, and titanium is higher melting than copper. Fusion of the latter is believed to have let water contact molten titanium [3].

See other VAPOUR EXPLOSIONS
See also MOLTEN METAL EXPLOSIONS
See other METALS, PYROPHORIC METALS

4914. Titanium salts

[16043-45-1] (4+) **TiZ_4**

Ti^{4+}

'Cupferron'

See Ammonium *N*-nitrosophenylaminooxide: Thorium salts

4915. Titanium—zirconium alloys

[50646-37-2] (1:1) **Ti—Zr**

Ti—Zr

See Zirconium (reference 6)
See other ALLOYS

4916. Thallium

[7440-28-0] **Tl**

Tl

Fluorine

See Fluorine: Metals
See other METALS

4917. Uranium

[7440-61-1] **U**

U

1. *MCA Case History No. 1296*
2. Bailar, 1973, Vol. 5, 40
3. Rieke, R. D. *et al., J. Org. Chem.*, 1979, **44**, 3446
4. Starks, D. F. *et al., J. Amer. Chem. Soc.*, 1973, **95**, 3423

Storage of uranium foil in closed containers in presence of air and water may produce a pyrophoric surface [1]. Uranium must be machined in a fume hood because, apart from the radioactivity hazard, the swarf is easily ignited. The massive metal ignites at 600—700°C in air [2]. The finely divided reactive form of uranium produced by pyrolysis of the hydride is pyrophoric [3], while that produced as a slurry by reduction of uranium tetrachloride in dimethoxyethane by potassium—sodium alloy is not [4].

Ammonia
Mellor, 1942, Vol. 12, 31
At dull red heat the metal incandesces in ammonia.

Bromine trifluoride
See Bromine trifluoride: Uranium, etc.

Carbon dioxide
Bailar, 1973, Vol. 5, 42
At 750°C interaction is so rapid that ignition will occur with the finely divided metal, and at 800°C the massive metal will ignite.

Carbon dioxide, Nitrogen
See Carbon dioxide: Metals, Nitrogen

Carbon tetrachloride
491M, 1975, 435
Use of a carbon tetrachloride fire extinguisher on a small uranium fire led to an explosion.
See other METAL—HALOCARBON INCIDENTS

Halogens
Mellor, 1942, Vol. 12, 31
Uranium powder ignites in fluorine at ambient temperature, in chlorine at 150—180°, in bromine vapour at 210—240° and in iodine vapour at 260°C.

Nitric acid, Trichloroethylene
MCA Case History No. 1104
Uranium scrap containing rather fine turnings was being pickled, after degreasing with trichloroethylene, by treatment with 4—6 M nitric acid solution. During subsequent rinsing with cold water, an explosion ejected the metal and acid liquor from the beaker. It has been reported in the literature that uranium reacts with nitric acid or dinitrogen tetraoxide either explosively, or with the formation of an explosive surface coating or residue. This corrosive effect is inhibited by presence of fluoride ion during pickling. Preventive measures proposed include separate treatment of finely divided uranium scrap, thorough pre-mixing of the acid solution and addition of ammonium hydrogen fluoride. An alternative, or contributory, cause could have been the violent reaction between dinitrogen tetraoxide and residual trichloroethylene.
See Dinitrogen tetraoxide: Halocarbons
See other CORROSION INCIDENTS

Nitrogen oxide
See Nitrogen oxide: Metals

Nitryl fluoride
See Nitryl fluoride: Metals

Selenium, or Sulfur
Mellor, 1942, Vol. 12, 31
Uranium incandesces in sulfur vapour, and with selenium also.

Water

See Magnesium: Water, Uranium

See other METALS, PYROPHORIC METALS

4918. Vanadium

[7440-62-2] **V**

V

Pascal, 1958, Vol. 12, 45

Some samples of vanadium prepared by magnesium reduction of vanadium dichloride or vanadium trichloride are pyrophoric.

Oxidants

See Bromine trifluoride: Halogens, etc.
Chlorine: Metals
Nitryl fluoride: Metals

See other METALS, PYROPHORIC METALS

4919. Tungsten

[7440-33-7] **W**

W

Mellor, 1943, Vol. 11, 729

The finely divided metal may ignite on heating in air.

Oxidants

1. Mellor, 1943, Vol. 11, 729
2. Rose, J. E., *Chem. Abs.*, 1980, **92**, 8483

The finely divided metal may ignite in contact with a range of oxidants, usually on heating [1]. Mixtures of the metal powder with barium chromate and potassium chlorate are used as a pyrotechnic fuse [2].

See Bromine: Tungsten, etc.
Bromine pentafluoride: Acids, etc.
Chlorine trifluoride: Metals
Fluorine: Metals
Hydrogen sulfide: Metals
Iodine pentafluoride: Metals
Lead(IV) oxide: Metals
Nitryl fluoride: Metals
Oxygen difluoride: Metals
Potassium dichromate: Tungsten
Potassium perchlorate: Barium chromate, etc.
Sodium peroxide: Metals

See other METALS, PYROPHORIC METALS

4920. Xenon

[7440-63-3] **Xe**

Xe

Sponsles, M. *et al., J. Amer. Chem. Soc.*, 1989, **111**(17), 6841

Liquid xenon, used as a solvent, will burst sealed apparatus if allowed to warm up. Pressure relief valves are recommended.

Fluorine

See Fluorine: Xenon

See other NON-METALS

4921. Zinc

[7440-66-6] **Zn**

Zn

NSC 267, 1978; *FPA H96*, 1980; *HCS 1980*, 966 (dust); *RSC Lab. Hazard Data Sheet No. 76*, 1988 (zinc and compounds)

1. Anon., *Chem. Ztg.*, 1940, 289
2. Anon., *Ind. Eng. Chem.*, 1944, **20**, 330
3. Robson, S., *School Sci. Rev.*, 1934, **16**(62), 165
4. Anon., *Jahresber.*, 1978, 72

A cloud of zinc dust generated by sieving the hot dried material exploded violently, apparently after initiation by a spark from the percussive sieve-shaking mechanism [1]. Precautions recommended include use of cold zinc and total enclosure of such processes [2]. The possibility of explosions of zinc dust suspended in air is presented as a serious hazard [3]. A serious dust explosion in the air filter unit of a zinc grinding mill was initiated by a spark from an explosion relief panel [4].

See Zinc chloride, below

Acetic acid

Wehrli, S., *Chem. Fabrik*, 1940, 362—363

The residues from zinc dust—acetic acid reduction operations may ignite after a long delay if discarded into waste-bins with paper. Small amounts appear to ignite more rapidly than larger portions.

See other PYROPHORIC MATERIALS

Aluminium

See Aluminium: Zinc

Aluminium, Magnesium, Rusted steel

See Aluminium—magnesium—zinc alloy: Rusted steel

Ammonium chloride, Water

1. Sorbe, 1968, 158
2. Hanson, R. M., *J. Chem. Educ.*, 1976, **53**, 578

A mixture of zinc dust with ammonium nitrate [1], or mixed nitrate and chloride [2] ignites when moistened.
See Ammonium nitrate: Metals

Ammonium nitrate, MRH 3.22/5
Ammonium sulfide
See Ammonium sulfide: Zinc

Arsenic alloy, Water
Carson. P. A. *et al., Loss Prev. Bull.* 1991, **102**, 7
An arsenic alloy in a galvanised container with water generated the extremely toxic gas arsine.
See Aluminium: Arsenic trioxide, Sodium arsenate, Sodium hydroxide
See Water, below

Arsenic trioxide
Mellor, 1940, Vol. 4, 486
A mixture with excess zinc filings explodes on heating

Calcium chloride
See Calcium chloride: Zinc

Carbon disulfide MRH 2.43/37
Mellor, 1940, Vol. 4, 4
Carbon disulfide and zinc powder interact with incandescence.

Carbon tetrachloride, MRH 2.43/54
Catalytic metals, Acids
Sidgwick, 1950, 1530, 2578
Alloys of zinc with iridium, platinum or rhodium, after extraction with acid, leave residues which explode on warming in air, owing to the presence of occluded hydrogen (or oxygen) in the catalytic metal powders so produced.

Chlorinated rubber
See Halocarbons (reference 2), below

Electrolytes, Silver
See Silver: Electrolytes, etc.

Ethyl acetoacetate, Tris(bromomethyl)ethanol
See Ethyl acetoacetate: 2,2,2-Tris(bromomethyl)ethanol, Zinc

Halocarbons MRH Carbon tetrachloride 2.43/54

1. Berger, E., *Compt. rend.*, 1920, **170**, 29
2. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 12
3. Lamouroux, A. *et al., Mém. Poudres*, 1957, **39**, 435—445

A paste of zinc powder and carbon tetrachloride (with kieselguhr as thickener) will readily burn after ignition by a high-temperature primer [1]. Intimate mixtures of chlorinated rubber with powdered zinc (or its oxide) in presence or absence of hydrocarbon or halocarbon solvents react violently or explosively at about 216°C

[2]. Powdered zinc initially reacts more violently with hexachloroethane in ethanol than does aluminium [3].
See Bromomethane: Metals
See also Chloromethane: Metals
See also CHLORINATED RUBBER: Metal oxides
See other METAL—HALOCARBON INCIDENTS

Halogens, or Interhalogens MRH Chlorine 3.05/52, fluorine 7.45/47
Mellor, 1940, Vol. 4, 476
Warm zinc powder incandesces in fluorine, and zinc foil ignites in cold chlorine if traces of moisture are present.
See Bromine pentafluoride: Acids, etc.
Chlorine trifluoride: Metals
Iodine: Metals, Water

Lead azide MRH 1.63/99+
See Lead(II) azide: Copper, etc.

Manganese dichloride
Terreill, A., *Bull. Soc. Chim. Fr. [2]*, 1874, **21**, 289
Zinc foil reacts explosively when heated with anhydrous manganese dichloride.

Metal oxides MRH Chromium trioxide 2.51/50, potassium peroxide 1.72/45
See Potassium dioxide: Metals
Titanium dioxide: Metals
Zinc peroxide: Alone, etc.

Methanol
See Methanol: Carbon tetrachloride, Metals

2-Nitroanisole, Sodium hydroxide
See 2-Nitroanisole: Sodium hydroxide, etc.

Nitrobenzene MRH 4.52/99+
Muir, G. D., private comm., 1968
Zinc residues from reduction of nitrobenzene to *N*-phenylhydroxylamine are often pyrophoric and must be kept wet during disposal.

Nitrogen compounds MRH values show % of nitrogen compound
See Hydrazinium nitrate: Alone, etc. MRH 1.67/50
Hydroxylamine: Metals MRH 3.85/99+

Non-metals MRH Sulfur 2.09/33
1. Mellor, 1940, Vol. 4, 480, 485
2. Read, C. W. W., *School Sci. Rev.*, 1940, **21**(83), 976

Arsenic, selenium and tellurium all react with incandescence on heating [1]. Interaction on heating powdered zinc and sulfur is considered to be too violent for use as a school experiment [2].

Other reactants

Yoshida, 1980, 1—2

MRH values calculated for 31 combinations, mainly with oxidants, are given.

Oxidants	MRH values show % of oxidant
See Halogens; Interhalogens; Metal oxides, all above	
Ammonium nitrate: Metals	MRH 3.22/55
Nitric acid: Metals	MRH 3.59/28
Nitryl fluoride: Metals	
Peroxyformic acid: Metals	MRH 5.69/99+
Potassium chlorate: Metals	MRH 3.63/38

Paint primer base

Muller, K. A., *Spontaneous Combustion of Zinc-rich Paint Mixtures*, Washington, API, 1969

Zinc residues from poorly mixed priming paint spontaneously inflamed after prolonged exposure to atmosphere. Aluminium residues may behave similarly.

Pentacarbonyliron, Transition metal halides

See Pentacarbonyliron: Transition metal halides, etc.

Seleninyl bromide

See Seleninyl bromide: Metals

Sodium hydroxide

1. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 14
2. Jackson, H., *Spectrum*, 1969, **7**(2), 82
3. *Summerlin, L. unpublished letter to Chem. Eng. News*, 1988

Accidental contamination of a metal scoop with flake sodium hydroxide, prior to its use with zinc dust, caused ignition of the latter [1]. A stiff paste prepared from zinc dust and 10% sodium hydroxide solution attains a temperature above 100°C after exposure to air for 15 min [2]. The residue of zinc dust and sodium hydroxide solution from a lecture demonstration involving zinc plating a copper coin presents a high fire risk if discarded onto paper in a waste bin, ignition of the paper having occurred on many occasions. Dissolve the residue in dilute acid before flushing away with water [3].

See Water, next below

See PAPER TOWELS

Water

1. Anon., *Metallwirtschaft*, 1941, **20**, 475
2. Anon., *Chem. Fabrik*, 1940, 362
3. Mellor, 1940, Vol 4, 474
4. Carson, P. J. *et al., Loss Prev. Bull.*, 1992, **102**, 15

In contact with atmospheric oxygen and limited amounts of water, zinc dust will generate heat, and may become incandescent [1]. Presence of acetic acid and copper shortens the induction period. Store the metal dry, and keep residues thoroughly wet until disposal [2]. Hydrogen is evolved, especially under acid or alkaline conditions [3]. An incident of a burst galvanised drum from hydrogen evolution is recorded [4].

See other CORROSION INCIDENTS, GAS EVOLUTION INCIDENTS, INDUCTION PERIOD INCIDENTS

Zinc chloride

Bylo, Z. *et al., Chem. Abs.*, 1983, **98**, 146031

Flammability of some commercial zinc dusts or powders is attributed to presence of zinc chloride.

See other METALS, PYROPHORIC METALS, REDUCANTS

4922. Zirconium

[7440-67-7] **Zr**

Zr

(*MCA SD-92*, 1966); *NSC 382*, 1968 (powder)

1. *Standard for Production, Processing, Handling and Storage of Zirconium*, NFPA 482M, 1974
2. *Zirconium Fire and Explosion Incidents*, TID-5365, Washington, USAEC, 1956
3. Gleason, R. P. *et al., J. Amer. Soc. Safety Eng.*, 1964, **9**(3), 15
4. Bulmer, G. H. *et al., Rept. AHSB(S) R59*, London, UKAEA, 1964
5. *MCA Case History No. 1234*
6. Ioffe, V. G., *Chem. Abs.*, 1967, **66**, 12614d
7. Karlowicz, P. *et al., J. Electrochem. Soc.*, 1961, **108**, 659—663
8. Leuschke, G. *et al., Chem. Abs.*, 1983, **98**, 221174
9. Baumgart, H., *Chem. Abs.*, 1985, **103**, 73412
10. Cooper, T D., *Chem. Abs.*, 1986, **104**, 65449
11. *See entry* DUST EXPLOSION INCIDENTS (reference 22)
12. Bond, 1991, 60

All aspects of hazards in the production, use and storage of zirconium are covered in a US Standard [1], and there is a compilation of 43 abstracts of unusual zirconium fire and explosion incidents, most of which involved the pyrophoric finely divided metal, moisture and friction, occasionally accompanied by the possibility of static sparks from polythene bags [2]. The increasing use of zirconium necessitated a review of methods of controlling the pronounced pyrophoric properties of zirconium powder. Five considerations for the safe use of zirconium include: exclusion of air or oxygen by use of inert gases; exclusion of water, its vapour and other contaminants or oxidants; control of particle size; limitation of amount of powder handled or exposed; and limitation of exposure of personnel [3]. Storage and disposal of irradiated metal wastes in various forms has also been discussed [4]. Ignition may not be immediate, however, as fine zirconium dust left uncleared from previous grinding operations was ignited violently by a spark from subsequent grinding operations [5]. The lower ignition limits of air suspensions of zirconium powder, of its alloys with silicon and titanium, and of zirconium—titanium hydride have been studied in relation to the history of exposure to air [6]. Treatment of zirconium powder with 1% hydrogen fluoride solution considerably desensitises it to electrostatic ignition [7]. Particles of Zircaloy (98—99% Zr) blown from tubes by compressed air ignited by friction or impact, even at 2 bar blow-off

pressure, and could initiate dust explosions [8]. Ignition and combustion properties of pyrotechnic zirconium and zirconium hydride powders (< 10 μ) and safety measures are discussed [9]. In a review of pyrophoricity of zirconium and its alloys, it emerged that the maximum particle size for pyrophoric behaviour is 54 μ, and that smaller particles may also explode as well as ignite in air. Factors influencing ignition temperature were explored, and recommendations made for safe handling, transportation and storage [10]. In dust explosions, maximum pressures of 5.1 bar, with maximum rates of rise of 748 bar/s have been determined [11]. Flakes of zirconium came away when a manhole cover was opened on a zirconium-distillation column containing methanol. The zirconium particles ignited, setting fire to the methanol vapour [12].
See Hafnium
See Lead—zirconium alloys
See METAL DUSTS, PYROPHORIC METALS

Carbon dioxide, Nitrogen
See Carbon dioxide: Metals, or: Metals, Nitrogen

Carbon tetrachloride
1. *Zirconium Fire and Explosion Incidents*, TID-5365, Washington, USAEC, 1956
2. *491M*, 1975, 446

A mixture of powdered zirconium and carbon tetrachloride exploded violently while being heated [1], and immersion of zirconium sponge in the unheated solvent also caused explosion [2].
See other METAL—HALOCARBON INCIDENTS

Nitryl fluoride
See Nitryl fluoride: Metals

Oxygen-containing compounds
1. Mellor, 1941, Vol. 7, 116
2. Ellern, 1968, 249

The affinity of zirconium for oxygen is great, particularly when the metal is finely divided, and extends to many oxygen-containing compounds. The vigorous reactions with potassium chlorate, potassium nitrate, copper(II) oxide or lead oxide might be anticipated, but there are also explosive reactions with the combined oxygen when zirconium is heated with alkali-metal hydroxides or carbonates, or even zirconium hydroxide. Hydrated sodium tetraborate behaves similarly [1]. Several alkali-metal oxosalts (chromates, dichromates, molybdates, sulfates, tungstates) react violently or explosively when reduced to the parent metals by heating with zirconium [2].
See Copper(II) oxide: Metals
Lead(II) oxide: Metals
Lithium chromate: Zirconium
Potassium chlorate: Metals
Potassium nitrate : Metals

Phosphorus
See Phosphorus: Metals

Sulfuric acid, Potassium bisulfate

Ullmann, 1996, A28, 554,

Zirconium powder mixed with an approximately equal quantity of 17% potassium bisulfate in concentrated sulfuric acid exploded violently.

See Oxygen-containing compounds above

Water

1. *MCA SD-92*, 1966
2. Muir, G. D., private comm., 1968
3. *Haz. Chem Data*, 1975, 305
4. Hall, A. N. *et al., Loss Prev. Bull.*, 1987, (076), 22—29

Powder damp with 5—10% of water may ignite, and although 25% of water is regarded as a safe concentration [1], ignition of a 50% paste on breakage of a glass container has been observed [2]. Although water is used to prevent ignition, the powder, once ignited, will burn under water (88.8% oxygen) more violently than in air (21% oxygen) [3]. The relatively minor part played by steam and zircalloy fuel containment cans (ruptured by the steam explosion) to form hydrogen towards the end of the catastrophic sequence involved in the Chernobyl nuclear reactor accident is noted in a comprehensive account of the causes of the disaster [4].

See other METALS, PYROPHORIC METALS

4923. Zirconium salts

[15543-40-5] **Zr^{4+}**

Zr^{4+}

‘Cupferron’

See Ammonium *N*-nitrosophenylaminooxide: Thorium salts

Appendix 1

Source Title Abbreviations used in Handbook References

The abbreviations used in the references for titles of journals and periodicals are those used in BP publications practice and conform closely to the recommendations of the *Chemical Abstracts* system. Abbreviations which have been used to indicate textbook and reference book sources of information are set out below with the full titles and publication details.

ABCM Quart. Safety Summ.,	*Quarterly Safety Summaries*, London, Association of British Chemical Manufacturers, 1930–1964
ACS 54, 1966	*Advanced Propellant Chemistry*, ACS 54, Washington, American Chemical Society, 1966
ACS 88, 1969	*Propellants Manufacture, Hazards and Testing*, ACS 88, Washington, American Chemical Society, 1969
Albright, Hanson, 1976	*Industrial and Laboratory Nitrations*, ACS Symposium Series 22, Albright, L. F., Hanson, C., (Eds.), Washington, American Chemical Society, 1976
Alkali Metals, 1957	*Alkali Metals*, ACS 19, Washington, American Chemical Society, 1957
ASHRAE. J.	*American Society of Heating, Refrigeration and Air-conditioning Engineers Journal*, New York.
Augustine, 1968	*Reduction, Techniques and Applications in Organic Chemistry*, Augustine, R. L., London, Edward Arnold, 1968

Augustine, 1969, 1971	*Oxidation, Techniques and Applications in Organic Synthesis*, Augustine, R. L., (Ed.), New York, Marcel Dekker, Vol. 1, 1968, Vol. 2 (with Trecker, D. J.), 1971
Bahme, 1972	*Fire Officer's Guide to Dangerous Chemicals*, FSP-36, Bahme, C. W., Boston, National Fire Protection Association, 1972
Bailar, 1973	*Comprehensive Inorganic Chemistry*, Bailar, J. C., Emeléus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., (Eds.), Oxford, Pergamon, 5 vols., 1973
BCISC Quart. Safety Summ.,	*Quarterly Safety Summaries*, London, British Chemical Industries Safety Council, 1965–1973
Barton & Ollis, 1979	*Comprehensive Organic Chemistry*, Barton, D. H. R., Ollis, W. D., (Eds), Oxford, Pergamon, 1979.
Biasutti, 1981	*History of Accidents in the Explosives Industry*, Biasutti, G. S. (Author and publisher), Vevey, 1981
Bond, 1991	*Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991
Braker, 1981	*Matheson Gas Data Book*, Braker, W., Mossman, A. L., Lyndhurst (NJ), Matheson Div. Searle, 6th edn. 1981
Brandsma, 1971	*Preparative Acetylenic Chemistry*, Brandsma, L., Barking, Elsevier, 1971
Brauer, 1961, 1965	*Handbook of Preparative Inorganic Chemistry*, Brauer, G., (Translation Ed. Riley, R. F.), London, Academic Press, 2nd edn. Vol. 1, 1963; Vol. 2, 1965
Bretherick, 1986	*Hazards in the Chemical Laboratory*, Bretherick, L. (Ed.), London, Royal Society of Chemistry, 4th edn., 1986
Castrantas, 1965	*Fire and Explosion Hazards of Peroxy Compounds*, Special Publication No. 394, Castrantas, H. M., Banerjee, D. K., Noller, D. C., Philadelphia, ASTM, 1965
Castrantas, 1970	*Laboratory Handling and Storage of Peroxy Compounds*, Special Publication No. 491, Castrantas, H. M., Banerjee, D. K., Philadelphia, ASTM, 1970

CHAS Notes	*Chemical Health and Safety Notes*, ACS Division of Chemical Health and Safety, Washington, 1982 to date (4 issues/yr)
Chemiarbeit	*Chemiearbeit, Schutzen und Helfen*, Dusseldorf, Berufsgenossenschaft der Chemische Industrie, 1949–1962 (supplement to Chemische Industrie)
Chem. Hazards Ind.	*Chemical Hazards in Industry*, Royal Society of Chemistry Information Group, Cambridge, 1984 to date (monthly abstracts)
CISHC Chem. Safety Summ.,	*Chemical Safety Summaries*, London, Chemical Industry Safety and Health Council of the Chemical Industries Association, 1974 to 1986 (terminated)
CHETAH 1990	*The ASTM Chemical Thermodynamic and Energy Release Evaluation Programme*, Version 4.4, 2nd Edn (ASTM Data Series Publication 51A), Davies C. A. *et al.*, Philadelphia, ASTM, Appendix V. Upgrades continue to be issued (1998)
Cloyd, 1965	*Handling Hazardous Materials*, Technical Survey No. SP-5032, Cloyd, D. R., Murphy, W. J., Washington, NASA, 1965
Coates, 1960	*Organometallic Compounds*, Coates, G. E., London, Methuen, 1960
Coates, 1967, 1968	*Organometallic Compounds*, Coates, G. E., Green, M. L. H., Wade, K., London, Methuen, Vol. 1, 1967, Vol. 2, 1968
Compendium 1985, 1987	*Compendium of Safety Data Sheets, for Research and Industrial Chemicals*, Keith, L. H., Walters, D. B., Deerfield Beach/Weinheim, VCH, vols. 1–3 of 867 sheets 1985, vols 4–6 of 723 sheets, 1987
Dangerous Loads, 1972	*Dangerous Loads*, Leicester, Institution of Fire Engineers, 1972
Dangerous Substances, 1972	*Dangerous Substances: Guidance on Fires and Spillages* (Section 1, ‘Inflammable liquids’), London, HMSO, 1972
Davies, 1961	*Organic Peroxides*, Davies, A. G., London, Butterworths, 1961
Davis, 1943	*Chemistry of Powder and Explosives*, Davis, T. L., New York, Wiley, 1943

DOC 5, 1982	*Dictionary of Organic Compounds*, Buckingham, J., (Ed.), London, Chapman & Hall, 5th edn. in 5 vols. + indices, 1982, annual supplementary vols. to date
Dunlop, 1953	*The Furans*, ACS 119, Dunlop, A. P., Peters, F. N., New York, Reinhold, 1953
Ellern, 1968	*Military and Civilian Pyrotechnics*, Ellern, H., New York, Chemical Publishing Co., 1968
Emeléus, 1960	*Modern Aspects of Inorganic Chemistry*, Emeléus, H. J., Anderson, J. S., London, Rutledge and Kegan Paul, 1960
Ephraim, 1939	*Inorganic Chemistry*, Ephraim, F., (3rd Engl. edn., Thorne, P. C. L., Ward, A. M.), London, Gurney & Jackson, 1939
Federoff, 1960	*Encyclopaedia of Explosives and Related Compounds*, Federoff, B. T. (Ed.), Dover (NJ), Piccatinny Arsenal, Vol. 1, 1960; Vol. 10, 1984 (from USNTIS)
Fieser, 1967–1986	*Reagents for Organic Synthesis*, Fieser, L. F. and Fieser, M., New York, Wiley, Vol. 1, 1967, The series continues after the death of the originator.
Freifelder, 1971	*Practical Catalytic Hydrogenation*, Freifelder, M., New York, Wiley-Interscience, 1971
Gallais, 1957	*Chimie Minérale Théoretique et Expérimental (Chimie Électronique)*, Gallais, F., Paris, Masson, 1957
Gaylord, 1956	*Reductions with Complex Metal Hydrides*, Gaylord, N. G., New York, Interscience, 1956
Gibson, 1969	*Handbook of Selected Properties of Air-and Water-Reactive Materials*, Gibson, H., Crane (In.), US Naval Ammunition Depot, 1969
Goehring, 1957	*Ergebnisse und Probleme der Chemie der Schwefelstickstoff-verbindung, Scientia Chemica*, Vol. 9, Goehring, M., Berlin, Akademie Verlag, 1957
Grignard, 1935–54	*Traité de Chimie Organique*, Grignard, V. and various volume Eds., Paris, Masson, Vol. 1, 1935, Vol. 23, 1954

Guide for Safety, 1972	*Guide for Safety in the Chemical Laboratory*, MCA, New York, Van Nostrand Reinhold, 2nd edn., 1972
Harmon, 1974	*A Review of Violent Monomer Polymerisation*, Harmon, M., King, J., Rept. AD-017443, Springfield (Va.), NTIS, 1974
Haz. Chem. Data, 1975	*Hazardous Chemical Data*, NFPA 49, Boston, National Fire Protection Association, 1975
HCS 1980	*Handling Chemicals Safely*, Dutch Assoc. of Safety Experts, Dutch Chemical Industry Assoc., Dutch Safety Inst., 1980 (Engl. transl. of 2nd Dutch edn.)
Houben-Weyl, 1953 to date	*Methoden der Organischen Chemie*, Müller, E. (Ed.), Stuttgart, Georg Thieme, 4th edn., published unsequentially from 1953.
Inorg. Synth., 1939–86	*Inorganic Syntheses*, various Eds., Maidenhead, McGraw-Hill, Vol. 1, 1939, Vol. 24, 1986
Jahresber. 1960 to date	*Jahresberichte*, Berufsgenossenschaft der Chemischen Industrie, Heidelberg, annually since 1960
JANAF, 1971	*JANAF Thermochemical Tables*, Stull, D. R., Prophet, H., National Bureau of Standards, 2nd edn., 1971
Karrer, 1950	*Organic Chemistry*, Karrer, P., London, Elsevier, 1950
Janz, 1976	*Eutectic Data, Table 2 (Safety Hazards, etc.)* Janz, G. J., Allen, C. B., Molten Salts Data Center, ERDA Rept. TID 27163-21, 1976; subsequently publ. in J. Haz. Mat., 1980–81, **4** (1), 145–176
Kharasch and Reinmuth, 1954	*Grignard Reactions of Non-Metallic Substances*, Kharasch, M. S. and Reinmuth, O., London, Constable, 1954
King, 1990	*Safety in the Process Industries*, King, R., London, Butterworth-Heinemann, 1990
Kirk-Othmer, 1963–71	*Encyclopaedia of Chemical Technology*, (3rd edn., 1978–83) Kirk, R. E., Othmer, D. F., London, Wiley-Interscience, Vol. 1, 1963, Vol. 22, 1970, Suppl. Vol. 1971. (4th edn., from 1991) 1993;

Kirshenbaum, 1956	*Final Report on Fundamental Studies of New Explosive Reactions*, Kirshenbaum, A. D., Philadelphia, Research Institute of Temple University, 1956
Kit and Evered, 1960	*Rocket Propellant Handbook*, Kit, B., Evered, D. S., London, MacMillan, 1960
Lab. Hazards Bull.	*Laboratory Hazards Bulletin*, Royal Society of Chemistry Information Group, Cambridge, 1981 to date (monthly abstracts)
Lawless, 1968	*High Energy Oxidisers*, Lawless, E. W. and Smith, I. C., New York, Marcel Dekker, 1968
Leleu, Cahiers, 1972–80	*Les Réactions Chimique Dangereuse*, Leleu, J., published serially in *Cahiers de Notes Documentaires*, from 1972 **(68)**, 319 to 1980, **(100)**, 426
Loss Prev. Bull., 1974 to date	*Loss Prevention Bulletin*, Rugby, Institution of Chemical Engineers, 6 issues annually since 1974
Mackay, 1966	*Hydrogen Compounds of the Metallic Elements*, Mackay, K. M., London, Spon, 1966
Major Loss Prevention, 1971	*Major Loss Prevention in the Process Industries, Symposium Series* No. 34, London, Institution of Chemical Engineers, 1971
Martin, 1971	*Dimethylsulfoxid*, Martin, D., Hauthal, H. G., Berlin, Akademie Verlag, 1971
Matheson Guide, 1982	*Guide to Safe Handling of Compressed Gases*, Matheson Div. Searle Medical Products, Lyndhurst (NJ), 1982
MCA Case Histories, 1950–78	*Case Histories of Accidents in the Chemical Industry*, Washington, MCA, (published monthly, republished as 4 ndexed collected volumes 1953–75, discontinued 1978)
(MCA SD-Series) 1947–76	*Safety Data Sheets*, MCA, Washington. The whole series of 101 sheets was withdrawn in 1980, but remains a useful source of collected information on basic industrial chemicals.
Meidl, 1972	*Hazardous Materials Handbook*, Meidl, J. H., Beverley Hills, Glencoe Press, 1972

Mellor, 1947–71	*Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Mellor, J. W., London, Longmans Green, Vol. 1, repr. 1941, Vol. 16, publ. 1937; and isolated Supplementary vols. up to Vol. 8 Suppl. 3, 1971
Mellor MIC, 1961	*Mellor's Modern Inorganic Chemistry*, Parkes, G. D. (Revision Ed.), London, Longmans Green, 1961
Merck, 1976, 1983, 1989, 1996	*The Merck Index*, Chapman and Hall, London., 9th edn. 1976, 10th edn. 1983, 11th edn. 1989, 12th edn. 1996
Merrifield, 1988	*Fire and Explosion Hazards associated with Storage and Handling of Hydrogen Peroxide*, Merrifield, R., Specialist Inspectors Report No. 19, Bootle, HSE. 1988
Meyer, 1977	*Chemistry of Hazardous Materials*, Meyer, E., Englewood Cliffs (NJ), Prentice-Hall, 1977
Miller, 1965–66	*Acetylene, its Properties, Manufacture and Uses*, Miller, S. A., London, Academic Press, Vol. 1, 1965, Vol. 2, 1966
Moissan, 1900	*Le Fluor et ses Composés*, Moissan, H., Paris, Steinheil, 1900
NFPA 491M, 1975	*Manual of Hazardous Chemical Reactions*, NFPA 491M, Quincy (MA), National Fire Potection Association, 5th edn., 1975 (larger format of same text, 1985)
Nolan, 1983	*Case Histories of Runaway Reactions*, Nolan, P. F., London, Polytechnic of the South Bank, 1983. A summary of the conclusions on the causes was published in *J. Haz. Materials*, 1987, **14**, 233–239
Org. Synth., 1941 to date	*Organic Syntheses*, various Eds., New York, Wiley, Collective Vol. 1, 1944; Coll. Vol. 2, 1944; Coll. Vol. 3, 1955; Coll. Vol. 4, 1962; Coll. Vol. 5, 1973; Coll. Vol. 6, 1987; Coll. Vol. 7, 1990; Coll. Vol. 8, 1993; annual volumes (from 70) thereafter.
Partington, 1967	*General and Inorganic Chemistry*, Partington, J. R., London, MacMillan, 4th edn., 1967

Pascal, 1956–70	*Nouveau Traité de Chimie Minérale*, Pascal, P. (Ed.), Paris, Masson, Vol. 1, 1956; Vol. 20.3, 1964; Vol. 15.5, 1970
Pieters, 1957	*Safety in the Chemical Laboratory*, Pieters, H. A. J., Creyghton, J. W., London, Academic Press, 2nd edn., 1957
Plant/Oper. Progress	*Plant Operations Progress* continues as *Process Safety Progress* 1993-
Pot. Incid. Rept.	*ASESB Potential Incident Report*, Washington, Armed Services Explosives Safety Board
Proc. nth Combust. Symp.	*Proceedings of Combustion Symposia*, various Eds. and Publishers, dated year following the event. 1st Symposium 1928; 19th Symposium, 1982
Renfrew, 1981	*Safety in the Chemical Laboratory*, Collected reprinted articles from *J. Chem. Educ.*, Renfrew, M. M. (Ed.), Vol. IV, 1981
Rodd, 1951–62	*The Chemistry of Carbon Compounds*, Rodd, E. H. (Ed.), London, Elsevier, Vol. 1A, 1951, Vol. 5, 1962; 2nd edn. began in 1979
RSC Data Sheets, 1982 to date	*Laboratory Hazard Data Sheet Series*, Cambridge, Royal Society of Chemistry, No. 1, 1982; No. 89, 1989, issued monthly, ceased 1993
RSC Safety Data Sheets, 1989	*Chemical Safety Data Sheets*, Cambridge, Royal Society of Chemistry, 1989 Generally similar to the monthly Laboratory Hazards Safety Data Sheet series, but the information is presented under headings reflecting legislative requirements. Volume 1 deals with some 100 largely organic liquid solvents and reagents, while Volume 2 covers main group metals and their compounds, 122 items in all. Vol. 3; Corrosives and Irritants, 1990. Vol 4; Toxic Chemicals, Pt. I 1990, Pt. II 1991. Vol 5, Flammables, 1989. There is considerable overlap among the volumes
Runaway Reactions, 1981	*Runaway Reactions, Unstable Products and Combustible Powders*, Symposium-Series No. 68 (Chester 1981), Rugby, Institution of Chemical Engineers, 1981

Rüst, 1948	*Unfälle beim Chemischen Arbeiten*, Rüst, E., Ebert, A., Zurich, Rascher Verlag, 2nd edn., 1948
Rutledge, 1968	*Acetylenic Compounds*, Rutledge, T. F., New York, Reinhold, 1968
Schmidt, 1967	*Handling and Use of Fluorine and Flourine-Oxygen Mixtures in Rocket Systems*, SP-3037, Schmidt, H. W., Harper, J. T., Washington, NASA, 1967
Schumacher, 1960	*Perchlorates, their Properties, Manufacture and uses*, ACS 146, Schumacher, J. C., New York, Reinhold, 1960
Schumb, 1955	*Hydrogen Peroxide*, ACS 128, Schumb, W. C., Satterfield, C. N., Wentworth, R. L., New York, Reinhold, 1955
Shriver, 1986	*Manipulation of Air-Sensitive Compounds*, Shriver, D. F. and Drozdzon, M. A. (Eds.), New York, Wiley, 2nd edn., 1986
Sichere Chemiearb.	*Sichere Chemiarbeit*, Heidelberg, Berufsgenossenschaft der Chemischen Industrie, 1963 to date
Sidgwick, 1950	*The Chemical Elements and their Compounds*, Sidgwick, N. V., Oxford, Oxford University Press, 1950
Sittig, 1981	*Handbook of Toxic and Hazardous Chemicals*, Sittig, M., Park Ridge (NJ), Noyes Data Corp., 2nd ed., 1985
Smith, 1965–6	*Open-Chain Nitrogen Compounds*, Smith, P. A. S., New York, Benjamin, Vol. 1, 1965; Vol. 2, 1966
Sorbe, 1968	*Giftige und Explosive Substanzen*, Sorbe, G., Frankfurt, Umschau Verlag, 1968
Steere, 1971	*Handbook of Laboratory Safety*, Steere, N. V. (Ed.), Cleveland, Chemical Rubber Publishing Co., 2nd edn., 1971. 3rd edn., Furr, A. K. (Ed.), 1989
Steere, 1967, ’71, ’74	*Safety in the Chemical Laboratory*, N. V. Steere (Ed.), Collected reprinted articles from *J. Chem. Educ.*, Vol. I, 1967; Vol. II, 1971; Vol. III, 1974

Stull, 1977	*Fundamentals of Fire and Explosion*, AIChE Monograph Series No. 10, Stull, D. R., New York, American Institute of Chemical Engineers, 1977
Swern, 1970–52	*Organic Peroxides*, Swern, D. (Ed.), London, Wiley-Interscience, Vol. 1, 1970; Vol. 2, 1971; Vol. 3, 1972
Ullmann, 1998	*Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, 6th edn. 1998 (CD update 1999)
Urbanski, 1964–84	*Chemistry and Technology of Explosives*, Urbanski, T., London, MacMillan, Vol. 1, 1964; Vol. 2, 1965; Vol. 3, 1967; Oxford, Pergamon, Vol. 4, 1984
Van Wazer, 1958–61	*Phosphorus and its Compounds*, Van Wazer, J. R., New York, Interscience, Vol. 1, 1958; Vol. 2, 1961
Vervalin, 1973	*Fire Protection Manual for Hydrocarbon Processing Plants*, Vervalin, C. H. (Ed.), Houston, Gulf Publishing Co., 2nd edn., 1973
Vogel, 1957	*A Textbook of Practical Organic Chemistry*, Vogel, A. I., London, Longmans Green, 3rd edn., 1957
von Schwartz, 1918	*Fire and Explosion Risks*, von Schwartz, E., London, Griffin, 1918
Weast, 1988	*Handbook of Chemistry and Physics*, Weast, R. C. (Ed.), Boca Raton (Fa.), CRC Press, 1988; continued under the editorship of Lide, D. R.
Whitmore, 1921	*Organic Compounds of Mercury*, Whitmore, F. C., New York, Chemical Catalog Co. Inc., 1921
Yoshida, 1980	*Handbook of Hazardous Reactions with Chemicals*, Yoshida, T., Tokyo, Tokyo Fire Department, 1980 (copy in British Library, Boston Spa)
Zabetakis, 1965	*Flammability Characteristics of Combustible Gases and Vapours*, Zabetakis, M. G., Washington, US Bureau of Mines, 1965

Appendix 2

Tabulated Fire-related Data

Compounds which are considered to be unusually hazardous in a fire context because of their low flash points (below 25°C) or auto-ignition temperatures (below 225°C) are included in the table. The names used are those titles in the text of Section 1 which are prefixed with a dagger. Synonyms may be found either in Section 1 or in the alphabetical index of chemical names and synonyms in Appendix 4. Boiling points are given for those compounds boiling below 50°C.

The figures for flash points are closed-cup values except where a suffix (o) indicates the (usually higher) open-cup value. The figures for explosive limits (or flammability limits) are % by volume in air at ambient temperature except where indicated otherwise. Where no figure has been found for the upper limit, a query has been inserted. Figures for auto-ignition temperatures are usually those determined in glass (without catalytic effects) except where stated.

Most of the values are those quoted in the references given in the topic entries:

AUTOIGNITION TEMPERATURES
FIRE
FLAMMABILITY
FLASH POINTS

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
Arsine	AsH_3	–62	—	flammable	—
Diborane	B_2H_6	–93	–90	0.9–98	38–52
Pentaborane(9)	B_5H_9	—	30	0.4–?	35
Bromosilane	BrH_3Si	2	< 0	—	ambient
Tribromosilane	Br_3HSi	112	—	flammable	ambient
Hydrogen cyanide	CHN	25.7	–18	6.0–41	—
Dichloromethane	CH_2Cl_2	39.7	calc –9	12.0–19.0	605
Difluoromethane	CH_2	–51		13–27	
Formaldehyde	CH_2O	–19	–19	7.0–73	—
Bromomethane	CH_3Br	3.5	none	see text	—
Chloromethane	CH_3Cl	–24	< 0	8.1–17	—
Methyltrichlorosilane	CH_3ClSi	—	8	7.6–?	—
Fluoromethane	CH_3F	–78	—	flammable	—
Methyl nitrite	CH_3NO_2	–12	—	flammable	explodes
Methane	CH_4	–161	–187	5.3–15	—
Dichloromethylsilane	CH_4Cl_2Si	—	–32	—	ambient
Methanol	CH_4O	—	10	6–36.5/60°	—
Methanethiol	CH_4S	6	–18	3.9–21.8	—
Methylamine	CH_5N	–6	–18	4.5–21	—
35%w/v in water		—	7.5	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
Methylhydrazine	CH_6N_2	—	18	2.5–97	194
Carbon monoxide	CO	–192	—	12.5–74	—
Carbonyl sulfide	COS	–50	—	12–28.2	—
Carbon disulfide	CS_2	46	–30	1.3–50	125 (below 100 if rust present)
Bromotrifluoroethylene	C_2BrF_3	–3	—	—	ambient
Chlorotrifluoroethylene	C_2ClF_3	–28	—	8.4–38.7	—
Tetrafluoroethylene	C_2F_4	–76	—	11–60	180
Trichloroethylene	C_2HCl_3	—	32 (above 30°C)	12.5–90	410
Trifluoroethylene	C_2HF_3	—	—	15.3–27	—
Acetylene	C_2H_2	–83	–18	2.5–82	—
1,1-Dichloroethylene	$C_2H_2Cl_2$	32	–15(o)	7.3–16	—
cis-1,2-Dichloroethylene	$C_2H_2Cl_2$	—	6	3.3–15	—
trans-1,2-Dichloroethylene	C_2HCl_2	4	2	9.7–12.8	—
1,1-Difluoroethylene	$C_2H_2F_2$	–86	—	5.5–21.3	—
Ethanedial	$C_2H_2O_2$	50	—	—	—
Bromoethylene	C_2H_3Br	16	< –8	6–16	—
Chloroethylene	C_2H_3Cl	–14	–8	4–22 (or 33)	—
1-Chloro-1,1-difluoroethane	$C_2H_3ClF_2$	−9	—	9–14.8	—
Acetyl chloride	C_2H_3ClO	—	4	5.0–?	—
Methyl chloroformate	$C_2H_3ClO_2$	—	12	—	—
1,1,1-Trichloroethane	$C_2H_3Cl_3$	—	none	8–10.5	500
Trichlorovinylsilane	$C_2H_3Cl_3Si$	—	–9	—	—
Fluoroethylene	C_2H_3F	−73	—	2.6–22	—
1,1,1-Trifluoroethane	$C_2H_3F_3$	−47	—	9.2–18.4	—
Acetonitrile	C_2H_3N	—	6(o)	4–16	—
Methyl isocyanate	C_2H_3NO 39	–7	—	—	—
Ethylene	C_2H_4	−104	−136	3.0–34	—
1,1-Dichloroethane	$C_2H_4Cl_2$	—	–6	5.6–11.4	—
1,2-Dichloroethane	$C_2H_4Cl_2$	—	13	6.2–15.9	—
Bis(chloromethyl) ether	$C_2H_4Cl_2O$	—	< 19	—	—
1,1-Difluoroethane	$C_2H_4F_2$	−25	—	3.7–18	—
Acetaldehyde	C_2H_4O	20	−38	4.0–57	204 (140 by DIN 51794)
Ethylene oxide	C_2H_4O	11	−20	3.0–100	—
Thiolacetic acid	C_2H_4OS	—	11	—	—
Methyl formate	$C_2H_4O_2$	32	−32	5.9–20	—
Thiiran	C_2H_4S	—	10	—	—
Bromoethane	C_2H_5Br	38	−20	6.7–11.3	—
Chloroethane	C_2H_5Cl	12	0	3.8–15.4	—
Chloromethyl methyl ether	C_2H_5ClO	—	−8	—	—
Trichloroethylsilane	$C_2H_5Cl_3Si$	—	14	—	—
Fluoroethane	C_2H_5F	−38	—	—	—
Aziridine	C_2H_5N	—	−11	3.3–54.8	—
Acetaldehyde oxime	C_2H_5NO	—	< 22	—	—
Ethyl nitrite	$C_2H_5NO_2$	17	35	3.1–>50	expl. >90
Ethyl nitrate	$C_2H_5NO_3$	—	10	3.8–?	expl. 85
Ethane	C_2H_6	−89	−93	3–12.5	—
Dichlorodimethylsilane	$C_2H_6Cl_2Si$	−9	—	3.4–9.5	—
Dichloroethylsilane	$C_2H_6Cl_2Si$	—	−1	—	—
Dimethyl ether	C_2H_6O	−24	−41	3.4–18 (27)	—
Ethanol	C_2H_6O	—	12	3.3–19/60°C	—
Dimethyl sulfoxide	C_2H_6OS	—	—	—	215
Dimethyl sulfate	$C_2H_6O_4S$	—	—	—	188
Dimethyl sulfide	C_2H_6S	37	−37	2.2–19.7	206
Ethanethiol	C_2H_6S	36	−17	2.8–18	—
Dimethyl disulfide	$C_2H_6S_2$	—	7	1.1–?	—
Dimethylamine	C_2H_7N	7	−50	2.8–14.4	—
40%w/v in water		—	−16	—	—
25%w/v in water		—	6	—	—
Ethylamine	C_2H_7N	17	−16	3.5–14	—
70%w/v in water		—	< 22	—	—
1,1-Dimethylhydrazine	$C_2H_8N_2$	—	1	2.1–95	—
1,2-Dimethylhydrazine	$C_2H_8N_2$	—	−17	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
1,1-Dimethyldiborane	$C_2H_{10}B_2$	−3	< −10	—	—
1,2-Dimethyldiborane	$C_2H_{10}B_2$	−49	< −55	—	—
Dicyanogen	C_2N_2	−21	—	6–32	—
Hexafluoropropene	C_3F_6	—	—	15–20	—
2-Chloroacrylonitrile	C_3H_2ClN	—	8	—	—
3-Bromopropyne	C_3H_3Br	—	10	3.0–?	—
3-Chloropropyne	C_3H_3Cl	—	−16	—	—
Acryloyl chloride	C_3H_3ClO	—	18	—	—
3,3,3-Trifluoropropene	$C_3H_3F_3$	−18	< −30	4.7–23.5	—
1,1,1-Trifluoroacetone	$C_3H_3F_3O$	22	−30	—	—
Acrylonitrile	C_3H_3Ne	—	−1	3.0–17	—
5%w/v in water		—	< 9	—	—
Isoxazole	C_3H_3NO	—	8	—	—
Oxazole	C_3H_3NO	—	18	—	—
Propadiene	C_3H_4	−34	—	1.7–12	—
Propyne	C_3H_4	−23	—	2.15–12.5	—
1-Chloro-3,3,3-trifluoropropane	$C_3H_4ClF_3$	—	—	6–14	—
2,3-Dichloropropene	$C_3H_4Cl_2$	—	10	—	—
Acrylaldehyde	C_3H_4O	—	−26	2.8–31	—
Methoxyacetylene	C_3H_4O	23	< −20	—	—
Vinyl formate	$C_3H_4O_2$	46	< 0	—	—
3-Bromo-1-propene	C_3H_5Br	—	−1	4.4–7.3	—
1-Chloro-1-propene	C_3H_5Cl	35	< −6	4.5–16	—
2-Chloropropene	C_3H_5Cl	22	−37	4.5–16	—
3-Chloropropene	C_3H_5Cl	45	−32	3.3–11.2	—
1-Chloro-2,3-epoxypropane	C_3H_5ClO	—	21	—	—
Propionyl chloride	C_3H_5ClO	—	12	—	—
Ethyl chloroformate	$C_3H_5ClO_2$	—	16	—	—
1-Fluoro-2,3-epoxypropane	C_3H_5FO	—	4	—	—
3-Iodopropene	C_3H_5I	—	5	—	—
Propiononitrile	C_3H_5N	—	6	3.1–?	—
Cyclopropane	C_3H_6	−33	—	2.4–10.4	—
Propene	C_3H_6	−48	−108	2.4–11.1 (see text)	—
1,1-Dichloropropane	$C_3H_6Cl_2$	—	21	3.1–?	—
1,2-Dichloropropane	$C_3H_6Cl_2$	—	15	3.4–14.5	—
Dichloromethylvinylsilane	$C_3H_6Cl_2Si$	—	−1	—	—
Acetone	C_3H_6O	—	−17	2.6–12.8	—
Methyl vinyl ether	C_3H_6O	5.5	−56(o)	2.6–39.0	—
Oxetane	C_3H_6O	50	−28	—	—
2-Propen-1-ol	C_3H_6O	—	21	3.0–18.0	—
Propionaldehyde	C_3H_6O	49	−9	2.9–17	207
Propylene oxide	C_3H_6O	34	−37	3.1–27.5	—
1,3-Dioxolane	$C_3H_6O_2$	—	2	—	—
Ethyl formate	$C_3H_6O_2$	—	−34	2.7–13.5	—
Methyl acetate	$C_3H_6O_2$	—	−9	3.1–16	—
Dimethyl carbonate	$C_3H_6O_3$	—	18	—	—
2-Propene-1-thiol	C_3H_6S	—	−10	—	—
1-Bromopropane	C_3H_7Br	—	−1	4.6–?	—
2-Bromopropane	C_3H_7Br	—	1	—	—
1-Chloropropane	C_3H_7Cl	47	< −18	2.6–11.1	—
2-Chloropropane	C_3H_7Cl	36	−32	2.8–10.7	—
Chloromethyl ethyl ether	C_3H_7ClO	—	15	—	—
2-Iodopropane	C_3H_7I	—	20	—	—
3-Aminopropene	C_3H_7N	—	−29	2.2–22	—
Azetidine	C_3H_7N	61	−20	—	—
Cyclopropylamine	C_3H_7N	—	1	—	—
2-Methylaziridine	C_3H_7N	—	−10	—	—
Isopropyl nitrite	$C_3H_7NO_2$	40	< 10	—	—
Propyl nitrite	$C_3H_7NO_2$	47	< 20	—	—
Isopropyl nitrate	$C_3H_7NO_3$	—	11	?–100	175
Propyl nitrate	$C_3H_7NO_3$	—	20	2–100	—
Propane	C_3H_8	7–45	−104	2.2–9.5	—
Ethyl methyl ether	C_3H_8O	11	−37	2–10.1	190
Propanol	C_3H_8O	—	15	2.5–13.5	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
2-Propanol	C_3H_8O	—	12	2.3–12.7	—
Dimethoxymethane	$C_3H_8O_2$	44	−18(o)	—	—
Ethyl methyl sulfide	C_3H_8S	—	−15	—	—
Propanethiol	C_3H_8S	—	−20	—	—
2-Propanethiol	C_3H_8S	—	−35	—	—
Trimethyl borate	$C_3H_9BO_3$	—	−8	—	—
Chlorotrimethylsilane	C_3H_9ClSi	—	−20	—	—
Iodotrimethylsilane	C_3H_9ISi	106	−31	—	—
Isopropylamine	C_3H_9N	32	−50	2.3–10.4	—
Propylamine	C_3H_9N	49	−37	2.0–10.4	—
Trimethylamine	C_3H_9N	3	−5	2.0–11.6	190
25%w/v in water		—	5	—	—
2-Methoxyetylamine	C_3HnNO	—	9	—	—
Trimethylsilyl azide	$C_3H_9N_3Si$	—	23	—	—
1,2-Diaminopropane	$C_3H_{10}N_2$	—	24	—	—
1,3-Diaminopropane	$C_3H_{10}N_2$	—	24(o)	—	—
Propadiene-1,3-dione	C_3O_2	7	—	6–30	—
1,3-Butadiyne	C_4H_2	10	—	1.4–100	—
Buten-3-yne	C_4H_4	5	< −5	1.8–40 (−93% in oxygen)	—
Furan	C_4H_4O	32	−36	2.3–14.3	—
Diketene	$C_4H_4O_2$	—	—	—	200
Methyl propiolate	$C_4H_4O_2$	—	10	—	—
Thiophene	C_4H_4S	—	−6	—	—
2-Chloro-1,3-butadiene	C_4H_5Cl	—	−20	2.5–20	—
Ethyl trifluoroacetate	$C_4H_5F_3O_2$	—	−17	—	—
1-Cyanopropene	C_4H_5N	—	16	—	—
3-Cyanopropene	C_4H_5N	—	19	—	—
1,2-Butadiene	C_4H_6	19	< 0	—	—
1,3-Butadiene	C_4H_6	−4	< −17	2–11.5	—
1-Butyne	C_4H_6	8	< −7	—	—
2-Butyne	C_4H_6	28	−31	1.4–?	—
Cyclobutene	C_4H_6	2	< −10	—	—
1-Buten-3-one	C_4H_6O	—	−7	2.1–15.6	—
Crotonaldehyde	C_4H_6O	—	13	2.1–15.5/60°	207
2,3-Dihydrofuran	C_4H_6O	54	−24	—	—
Divinyl ether	C_4H_6O	29	< −30	1.7–27	—
3,4-Epoxybutene	C_4H_6O	—	< −50	—	—
Ethoxyacetylene	C_4H_6O	50	< −7	—	—
Methacrylaldehyde	C_4H_6O	—	−15	—	—
Allyl formate	$C_4H_6O_2$	—	< 22	—	—
Butane-2,3-dione	$C_4H_6O_2$	—	7	—	—
1,2:3,4-Diepoxybutane	$C_4H_6O_2$	—	−10	—	—
Methyl acrylate	$C_4H_6O_2$	—	−3(o)	2.8–25	—
Vinyl acetate	$C_4H_6O_2$	—	−8	2.6–13.4	—
1-Bromo-2-butene	C_4H_7Br	—	13	—	—
4-Bromo-1-butene	C_4H_7Br	—	1	—	—
2-Chloro-2-butene	C_4H_7Cl	—	−25	2.3–9.3	—
3-Chloro-1-butene	C_4H_7Cl	—	−27	2.2–?	—
3-Chloro-2-methyl-1-propene	C_4H_7Cl	—	−19	2.3–9.3	—
Butyryl chloride	C_4H_7ClO	—	18	—	—
2-Chloroethyl vinyl ether	C_4H_7ClO	—	25	—	—
Isobutyryl chloride	C_4H_7ClO	—	8	—	—
Isopropyl chloroformate	$C_4H_7ClO_2$	—	11	—	—
Butyronitrile	C_4H_7N	—	21	—	—
Isobutyronitrile	C_4H_7N	—	8	—	—
2-Methyl-2-oxazoline	C_4H_7NO	—	20	—	—
1-Butene	C_4H_8	−6	−80	1.6–9.3	—
cis-2-Butene	C_4H_8	4	−12	1.7–9.7	—
trans-2-Butene	C_4H_8	3	< −6	1.8–9.7	—
Cyclobutane	C_4H_8	13	< 10	1.8–?	—
Methylcyclopropane	C_4H_8	4	< 0	—	—
2-Methylpropene	C_4H_8	−7	< −10	1.8–8.8	—
mixo-Dichlorobutane	$C_4H_8Cl_2$	—	21	—	—
2-Butanone	C_4H_8O	—	−1	1.8–11.5	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
Butyraldehyde	C_4H_8O	—	−6	2.5–?	230
Cyclopropyl methyl ether	C_4H_8O	—	< 10	—	—
1,2-Epoxybutane	C_4H_8O	44.7	−15	1.5–18.3	—
Ethyl vinyl ether	C_4H_8O	36	−46	1.7–29	202
Isobutyraldehyde	C_4H_8O	—	−25	1.6–10.6	223
Tetrahydrofuran	C_4H_8O	—	−17	1.8–11.8	224
1,3-Dioxane	$C_4H_8O_2$	—	2(o)	2–22	—
1,4-Dioxane	$C_4H_8O_2$	—	12	2–22	180
Ethyl acetate	$C_4H_8O_2$	—	−4	2.2–11.5	—
Isopropyl formate	$C_4H_8O_2$	—	−6	—	—
Methyl propionate	$C_4H_8O_2$	—	−2	2.5–13	—
Propyl formate	$C_4H_8O_2$	—	−3	2.3–?	—
Tetrahydrothiophene	C_4H_8S	—	13	—	—
1-Bromobutane	C_4H_9Br	—	18	2.8–6.6/100	—
2-Bromobutane	C_4H_9Br	—	21	—	—
1-Bromo-2-methylpropane	C_4H_9Br	—	22	—	—
2-Bromo-2-methylpropane	C_4H_9Br	—	−18	—	—
2-Bromoethyl ethyl ether	C_4H_9BrO	—	21	—	—
1-Chlorobutane	C_4H_9Cl	—	−12	1.9–10.1	—
2-Chlorobutane	C_4H_9Cl	—	−10	—	—
1-Chloro-2-methylpropane	C_4H_9Cl	—	−6	2.0–8.7	—
2-Chloro-2-methylpropane	C_4H_9Cl	—	0	—	—
2-Iodobutane	C_4H_9I	—	−10	—	—
1-Iodo-2-methylpropane	C_4H_9I	—	0	—	—
2-Iodo-2-methylpropane	C_4H_9I	—	−10	—	—
Pyrrolidine	C_4H_9N	—	3	—	—
Butyl nitrite	$C_4H_9NO_2$	—	10	—	—
tert-Butyl nitrite	$C_4H_9NO_2$	—	−13	—	—
Cyanotrimethylsilane	C_4H_9NSi	114	1	—	—
Butane	C_4H_{10}	1	−60	1.9–8.5	—
Isobutane	C_4H_{10}	−12	−81	1.9–8.5	—
Dichlorodiethylsilane	$C_4H_{10}Cl_2Si$	—	24	—	—
2-Butanol	$C_4H_{10}O$	—	14	(1.7–9.8/100°)	—
tert-Butanol	$C_4H_{10}O$	—	10	2.4–8	—
Diethyl ether	$C_4H_{10}O$	36	−45	1.8–36.5	180
Methyl propyl ether	$C_4H_{10}O$	39	−20	2.0–14.8	—
1,1-Dimethoxyethane	$C_4H_{10}O_2$	—	1(o)	—	—
1,2-Dimethoxyethane	$C_4H_{10}O_2$	—	1	—	—
Trimethyl orthoformate	$C_4H_{10}O_3$	—	15	—	—
1-Butanethiol	$C_4H_{10}S$	—	2	—	—
2-Butanethiol	$C_4H_{10}S$	—	−23	—	—
Diethyl sulfide	$C_4H_{10}S$	—	−10	—	—
2-Methylpropanethiol	$C_4H_{10}S$	—	−10	—	—
2-Methyl-2-propanethiol	$C_4H_{10}S$	< −29	—	—	—
Butylamine	$C_4H_{11}N$	—	−12	1.7–9.8	—
2-Butylamine	$C_4H_{11}N$	—	−9	—	—
tert-Butylamine	$C_4H_{11}N$	45	−7	(1.7–9.8/100°)	—
Diethylamine	$C_4H_{11}N$	—	−39	1.8–10.1	—
Ethyldimethylamine	$C_4H_{11}N$	—	−36	—	—
Isobutylamine	$C_4H_{11}N$	—	−9	—	—
2-Dimethylaminoethylamine	$C_4H_{12}N$	—	11	—	—
Tetramethyl orthosilicate	$C_4H_{12}O_4Si$	—	20	—	—
Tetramethylsilane	$C_4H_{12}Si$	26	< 0	—	—
Tetramethyltin	$C_4H_{12}Sn$	—	−12	1.9–?	—
Dicyanoacetylene	C_4N_2	76	—	—	130
Tetracarbonylnickel	C_4NiO_4	43	< −20	2.0–?	—
Pentacarbonyliron	C_5FeO_5	—	−15	—	ambient
Pyridine	C_5H_5N	—	20	1.8–12.4	—
Cyclopentadiene	C_5H_6	42	−3	—	—
2-Methyl-1-buten-3-yne	C_5H_6	—	< −7(o)	—	—
2-Methylfuran	C_5H_6O	—	−30	—	—
2-Methylthiophene	C_5H_6S	—	8	—	—
1-Methylpyrrole	C_5H_7N	—	16	—	—
Cyclopentene	C_5H_8	44	−29	—	—
3-Methyl-1,2-butadiene	C_5H_8	40	−12	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
2-Methyl-1,3-butadiene	C_5H_8	34	−53	2.0–8.9	220
3-Methyl-1-butyne	C_5H_8	29.3	—	—	—
1,2-Pentadiene	C_5H_8	44.9	—	—	—
1,3-Pentadiene	C_5H_8	42	−43	2–8.3	—
1,4-Pentadiene	C_5H_8	26	4	—	—
1-Pentyne	C_5H_8	—	−20	—	—
2-Pentyne	C_5H_8	56	—	—	—
Allyl vinyl ether	C_5H_8O	—	< 21(o)	—	—
Cyclopentene oxide	C_5H_8O	—	10	—	—
Cyclopropyl methyl ketone	C_5H_8O	—	13	—	—
2,3-Dihydropyran	C_5H_8O	—	−16	—	—
2-Methyl-3-butyn-2-ol	C_5H_8O	—	20	—	—
Methyl isopropenyl ketone	C_5H_8O	—	21	(1.8–9.0/50°)	—
Allyl acetate	$C_5H_8O_2$	—	22	—	—
Ethyl acrylate	$C_5H_8O_2$	—	9	1.8–?	—
Methyl crotonate	$C_5H_8O_2$	—	−1	—	—
Methyl cyclopropanecarboxylate	$C_5H_8O_2$	—	17	—	—
Methyl methacrylate	$C_5H_8O_2$	—	8	2.1–12.5	—
Isopropenyl acetate	$C_5H_8O_2$	—	16	1.9–?	—
Vinyl propionate	$C_5H_8O_2$	—	1	—	—
Chlorocyclopentane	C_5H_9Cl	—	16	—	—
Pivaloyl chloride	C_5H_9ClO	—	8	—	—
Pivalonitrile	C_5H_9N	—	21	—	—
1,2,3,6-Tetrahydropyridine	C_5H_9N	—	16	—	—
Butyl isocyanate	C_5H_9NO	—	11	—	—
Cyclopentane	C_5H_{10}	49	−25	—	—
1,1-Dimethylcyclopropane	C_5H_{10}	20	—	—	—
Ethylcyclopropane	C_5H_{10}	36	< 10	—	—
2-Methyl-1-butene	C_5H_{10}	39	−20	—	—
2-Methyl-2-butene	C_5H_{10}	38	−20	—	—
3-Methyl-1-butene	C_5H_{10}	20	−7	1.5–9.1	—
Methylcyclobutane	C_5H_{10}	41	< 10	—	—
1-Pentene	C_5H_{10}	30	−18	1.5–8.7	—
2-Pentene	C_5H_{10}	30	−18	—	—
Allyl ethyl ether	$C_5H_{10}O$	—	−20	—	—
Ethyl propenyl ether	$C_5H_{10}O$	—	< −5	—	—
Isopropyl vinyl ether	$C_5H_{10}O$	—	−32	—	—
Isovaleraldehyde	$C_5H_{10}O$	—	−5	—	—
3-Methyl-2-butanone	$C_5H_{10}O$	—	−3	—	—
2-Methyl-3-butene-2-ol	$C_5H_{10}O$	—	18	—	—
2-Methyltetrahydrofuran	$C_5H_{10}O$	—	−12	—	—
2-Pentanone	$C_5H_{10}O$	—	7	1.6–7.2	—
3-Pentanone	$C_5H_{10}O$	—	13	1.6–?	—
4-Penten-2-ol	$C_5H_{10}O$	—	25	—	—
Tetrahdropyran	$C_5H_{10}O$	—	−20	—	—
Valeraldehyde	$C_5H_{10}O$	—	12	—	—
Butyl formate	$C_5H_{10}O_2$	—	18	1.7–8	—
3,3-Dimethoxypropene	$C_5H_{10}O_2$	—	19	—	—
2,2-Dimethyl-1,3-dioxolane	$C_5H_{10}O_2$	—	−1	—	—
Ethyl propionate	$C_5H_{10}O_2$	—	12	1,9–11	—
Isobutyl formate	$C_5H_{10}O_2$	—	5	2.0–8.9	—
Isopropyl acetate	$C_5H_{10}O_2$	—	4	1.7–7.8	—
2-Methoxyethyl vinyl ether	$C_5H_{10}O_2$	—	18(o)	—	—
Methyl butyrate	$C_5H_{10}O_2$	—	14	—	—
4-Methyl-1,3-dioxane	$C_5H_{10}O_2$	—	16	—	—
Methyl isobutyrate	$C_5H_{10}O_2$	—	13(o)	—	—
Propyl acetate	$C_5H_{10}O_2$	—	14	1.7–8	—
Diethyl carbonate	$C_5H_{10}O_3$	—	25	—	—
1-Bromo-3-methylbutane	$C_5H_{11}Br$	—	21	—	—
2-Bromopentane	$C_5H_{11}Br$	—	20	—	—
1-Chloro-3-methylbutane	$C_5H_{11}Cl$	—	< 21	1.5–7.4	—
2-Chloro-2-methylbutane	$C_5H_{11}Cl$	—	3	1.5–7.4	—
1-Chloropentane	$C_5H_{11}Cl$	—	1	1.6–8.6	—
2-Iodopentane	$C_5H_{11}I$	—	< 23	—	—
Cyclopentylamine	$C_5H_{11}N$	—	13	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
1-Methylpyrrolidine	$C_5H_{11}N$	—	3	—	—
Piperidine	$C_5H_{11}N$	—	3	—	—
4-Methylmorpholine	$C_5H_{11}NO$	—	24	—	—
Isopentyl nitrite	$C_5H_{11}NO_2$	—	−18	1–? (calc.)	209
Pentyl nitrite	$C_5H_{11}NO_2$	—	< 23	—	—
2,2-Dimethylpropane	C_5H_{12}	9	< −7	1.4–7.5	—
2-Methylbutane	C_5H_{12}	28	−51	1.4–7.6	—
Pentane	C_5H_{12}	36	−40	1.4–8.0	—
Butyl methyl ether	$C_5H_{12}O$	—	−10	—	—
tert-Butyl methyl ether	$C_5H_{12}O$	55	−28	2.5–15.1	—
Ethyl isopropyl ether	$C_5H_{12}O$	—	< −15	—	—
Ethyl propyl ether	$C_5H_{12}O$	—	< −20	1.7–9	—
tert-Pentanol	$C_5H_{12}O$	—	19	1.2–9	—
Diethoxymethane	$C_5H_{12}O_2$	—	o55	—	—
1,1-Dimethoxypropane	$C_5H_{12}O_2$	—	< 10	—	—
2,2-Dimethoxypropane	$C_5H_{12}O_2$	—	−7	—	—
Tetramethyl orthocarbonate	$C_5H_{12}O_4$	—	6	—	—
2-Methyl-2-butanethiol	$C_5H_{12}S$	—	−1	—	—
3-Methylbutanethiol	$C_5H_{12}S$	—	18	—	—
Pentanethiol	$C_5H_{12}S$	—	18	—	—
1,1-Dimethylpropylamine	$C_5H_{13}N$	—	−1	—	—
1,2-Dimethylpropylamine	$C_5H_{13}N$	—	−20	—	—
2,2-Dimethylpropylamine	$C_5H_{13}N$	—	25	—	—
N,N-Dimethylpropylamine	$C_5H_{13}N$	—	−11	—	—
Isopentylamine	$C_5H_{13}N$	—	−1	2.3–22	—
N-Methylbutylamine	$C_5H_{13}N$	—	2	—	—
Pentylamine	$C_5H_{13}N$	—	−1	—	—
2-Dimethylamino-*N*-methyl-ethylamine	$C_5H_{14}N_2$	—	14	—	—
Dimethylaminotrimethylsilane	$C_5H_{15}NSi$	—	−19	—	—
Hexafluorobenzene	C_6F_6	—	10	—	—
1,2,4,5-Tetrafluorobenzene	$C_6H_2F_4$	—	4(o)	—	—
1,2,4-Trifluorobenzene	$C_6H_3F_3$	—	−5(o)	—	—
2-, 3-, or 4-Chlorofluorobenzene	C_6H_4ClF	—	all 18	—	—
1,3-Difluorobenzene	$C_6H_4F_2$	—	< 0	—	—
1,4-Difluorobenzene	$C_6H_4F_2$	—	−5(o)	—	—
Fluorobenzene	C_6H_5F	—	−15	—	—
Benzene	C_6H_6	—	−11	1.4–8.0	—
1,5-Hexadien-3-yne	C_6H_6	—	< −20	1.5–?	—
1,3-Cyclohexadiene	C_6H_8	—	−6	—	—
1,4-Cyclohexadiene	C_6H_8	—	−11	—	—
2,5-Dimethylfuran	C_6H_8O	—	16	—	—
Cyclohexene	C_6H_{10}	—	−12	1.2–?/100°	310
1,3-Hexadiene	C_6H_{10}	—	−3	—	—
1,4-Hexadiene	C_6H_{10}	—	−21	2.0–6.1	—
1,5-Hexadiene	C_6H_{10}	—	−46	—	—
c- or t-2-*trans*-4-Hexadiene	C_6H_{10}	—	−7	—	—
1-, 2- or 3-Hexyne	C_6H_{10}	—	−10	—	—
2-Methyl-1,3-pentadiene	C_6H_{10}	—	−12	—	—
4-Methyl-1,3-pentadiene	C_6H_{10}	—	−34	—	—
Diallyl ether	$C_6H_{10}O$	—	−6	—	—
3-Methyl-2-methylenebutanal	$C_6H_{10}O$	—	11	—	—
Ethyl crotonate	$C_6H_{10}O_2$	—	2	—	—
Ethyl cyclopropanecarboxylate	$C_6H_{10}O_2$	—	18	—	—
Ethyl methacrylate	$C_6H_{10}O_2$	—	21	1.8–?	—
Vinyl butyrate	$C_6H_{10}O_2$	—	21(o)	1.4–8.8	—
Diallylamine	$C_6H_{11}N$	—	15	—	—
Cyclohexane	C_6H_{12}	—	−20	1.3–8.4	—
Ethylcyclobutane	C_6H_{12}	—	−15	1.2–7.7	210
1-Hexene	C_6H_{12}	—	−26	1.2–6.9	—
2-Hexene	C_6H_{12}	—	−21	—	—
Methylcyclopentane	C_6H_{12}	—	−29	—	—
2-Methyl-1-pentene	C_6H_{12}	—	−28	—	—
4-Methyl-1-pentene	C_6H_{12}	—	−7	—	—
cis 8-4-Methyl-2-pentene	C_6H_{12}	—	−32	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
trans 8-4-Methyl-2-pentene	C_6H_{12}	—	−29	—	—
Butyl vinyl ether	$C_6H_{12}O$	—	−1	—	—
3,3-Dimethyl-2-butanone	$C_6H_{12}O$	—	12	—	—
2-Ethylbutyraldehyde	$C_6H_{12}O$	—	21	1.2–7.7	—
2-Hexanone	$C_6H_{12}O$	—	23	1.2–8.0	—
3-Hexanone	$C_6H_{12}O$	—	14	—	—
Isobutyl vinyl ether	$C_6H_{12}O$	—	−9	—	—
2-Methylpentanal	$C_6H_{12}O$	—	20	—	195
3-Methylpentanal	$C_6H_{12}O$	—	< 23	—	—
2-Methyl-3-pentanone	$C_6H_{12}O$	—	1	—	—
3-Methyl-2-pentanone	$C_6H_{12}O$	—	15	—	—
4-Methyl-2-pentanone	$C_6H_{12}O$	—	17	1.2–8	—
Butyl acetate	$C_6H_{12}O_2$	—	23	1.4–7.5	—
2-Butyl acetate	$C_6H_{12}O_2$	—	18	1.3–7.5	—
2,6-Dimethyl-1,4-dioxane	$C_6H_{12}O_2$	—	24	—	—
Ethyl isobutyrate	$C_6H_{12}O_2$	—	13	—	—
2-Ethyl-2-methyl-1,3-dioxolane	$C_6H_{12}O_2$	—	23(o)	—	—
4-Hydroxy-4-methyl-2-pentanone	$C_6H_{12}O_2$	—	9	—	—
Isobutyl acetate	$C_6H_{12}O_2$	—	17	2.4–10.5	—
Isopentyl formate	$C_6H_{12}O_2$	—	23	1.2–8.0	—
Isopropyl propionate	$C_6H_{12}O_2$	—	21	—	—
Methyl isovalerate	$C_6H_{12}O_2$	—	20	—	—
Methyl pivalate	$C_6H_{12}O_2$	—	7	—	—
Methyl valerate	$C_6H_{12}O_2$	—	< 25	—	—
Isobutyl peroxyacetate	$C_6H_{12}O_3$	—	< 25	—	—
2,4,6-Trimethyltrioxane	$C_6H_{12}O_3$	—	17	1.3–?	—
Cyclohexylamine	$C_6H_{13}N$	—	21	—	—
1-Methylpiperidine	$C_6H_{13}N$	—	3	—	—
2-Methylpiperidine	$C_6H_{13}N$	—	10	—	—
3-Methylpiperidine	$C_6H_{13}N$	—	8	—	—
4-Methylpiperidine	$C_6H_{13}N$	—	9	—	—
Perhydroazepine	$C_6H_{13}N$	—	22	—	—
2,2-Dimethylbutane	C_6H_{14}	50	−48	(1.2–7.0/100°)	—
2,3-Dimethylbutane	C_6H_{14}	—	−29	1.2–7.0	—
Hexane	C_6H_{14}	—	−23	1.1–7.5	225
Isohexane	C_6H_{14}	—	−7	1.2–7.0	—
3-Methylpentane	C_6H_{14}	—	−7	1.2–7.0	—
Butyl ethyl ether	$C_6H_{14}O$	—	−1	—	—
tert-Butyl ethyl ether	$C_6H_{14}O$	—	−19	—	—
Diisopropyl ether	$C_6H_{14}O$	—	−36	1.4–21	—
Dipropyl ether	$C_6H_{14}O$	—	−21	—	215
2-Methyl-2-pentanol	$C_6H_{14}O$	—	21	—	—
1,1-Diethoxyethane	$C_6H_{14}O_2$	—	−21	1.7–10.4	—
1,2-Diethoxyethane	$C_6H_{14}O_2$	—	—	—	205
Triethylaluminium	$C_6H_{15}Al$	—	< −53	—	< −53
Triethyl borate	$C_6H_{15}BO_3$	—	11	—	—
Butylethylamine	$C_6H_{15}N$	—	18(o)	—	—
Diisopropylamine	$C_6H_{15}N$	—	−7	—	—
1,3-Dimethylbutylamine	$C_6H_{15}N$	—	13	—	—
Dipropylamine	$C_6H_{15}N$	—	17	—	—
Triethylamine	$C_6H_{15}N$	—	−7	1.2–8.0	—
1,2-Bis(dimethylamino)ethane	$C_6H_{16}N_2$	—	18	—	—
Diethoxydimethylsilane	$C_6H_{16}O_2Si$	—	11	—	—
Bis(trimethylsilyl) oxide	$C_6H_{18}OSi_2$	—	−1	—	—
Hexamethyldisilazane	$C_6H_{19}NSi_2$	—	14	—	—
Benzaldehyde	C_7H_6O	—	—	—	190
2-Fluorotoluene	C_7H_7F	—	8	—	—
3-Fluorotoluene	C_7H_7F	—	12	—	—
4-Fluorotoluene	C_7H_7F	—	10	—	—
Bicyclo[2.2.1]-2,5-heptadiene	C_7H_8	—	−21	—	—
1,3,5-Cycloheptatriene	C_7H_8	—	4	—	—
Toluene	C_7H_8	—	4	1.3–7.0	—
Cycloheptene	C_7H_{12}	—	−6	—	—
1-Heptyne	C_7H_{12}	—	−2	—	—
4-Methylcyclohexene	C_7H_{12}	—	−1(o)	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
Cycloheptane	C_7H_{14}	—	6	—	—
Ethylcyclopentane	C_7H_{14}	—	15	1.1–6.7	—
1-Heptene	C_7H_{14}	—	−1	—	—
2-Heptene	C_7H_{14}	—	< −1	—	—
3-Heptene	C_7H_{14}	—	< −7	—	—
Methylcyclohexane	C_7H_{14}	—	−4	1.2–6.7	—
2,3,3-Trimethylbutene	C_7H_{14}	—	< 0	—	—
2,4-Dimethyl-3-pentanone	$C_7H_{14}O$	—	15	—	—
3,3-Diethoxypropene	$C_7H_{14}O_2$	—	4	—	—
Ethyl isovalerate	$C_7H_{14}O_2$	—	25	—	—
Isobutyl propionate	$C_7H_{14}O_2$	—	18	—	—
Isopentyl acetate	$C_7H_{14}O_2$	—	25	(1.1–7.0/100°)	—
Isopropyl butyrate	$C_7H_{14}O_2$	—	24	—	—
Isopropyl isobutyrate	$C_7H_{14}O_2$	—	20	—	—
Pentyl acetate	$C_7H_{14}O_2$	—	25	1.1–7.5	—
2-Pentyl acetate	$C_7H_{14}O_2$	—	23	1.1–7.5	—
2,6-Dimethylpiperidine	$C_7H_{15}N$	—	16	—	—
1-Ethylpiperidine	$C_7H_{15}N$	—	19	—	—
2-Ethylpiperidine	$C_7H_{15}N$	—	−12	—	—
2,3-Dimethylpentane	C_7H_{16}	—	−56	1.1–6.7	—
2,4-Dimethylpentane	C_7H_{16}	—	−12	—	—
Heptane	C_7H_{16}	—	−4	1.2–6.7	223
2-Methylhexane	C_7H_{16}	—	−1	1.0–6.0	—
3-Methylhexane	C_7H_{16}	—	−1	1.0–6.0	—
2,2,3-Trimethylbutane	C_7H_{16}	—	−20	1.0–?	—
Phenylglyoxal	$C_8H_6O_2$	—	< 23	—	—
1,3,5,7-Cyclooctatetraene	C_8H_8	—	21	—	—
Ethylbenzene	C_8H_{10}	—	15	1.2–6.8	—
o-Xylene	C_8H_{10}	—	17	1.0–6.0	—
m- or p-Xylene	C_8H_{10}	—	25	1.1–7.0	—
4-Vinylcyclohexene	C_8H_{12}	—	16	—	—
1,7-Octadiene	C_8H_{14}	—	25	—	—
1-Octyne	C_8H_{14}	—	16	—	—
2-, 3-, or 4-Octyne	C_8H_{14}	—	all < 23	—	—
Vinylcyclohexane	C_8H_{14}	—	16	—	—
cis-1,2-Dimethylcyclohexane	C_8H_{16}	—	11	—	—
trans-1,2-Dimethylcyclohexane	C_8H_{16}	—	7	—	—
1,3-Dimethylcyclohexane	C_8H_{16}	—	6	—	—
cis-1,4-Dimethylcyclohexane	C_8H_{16}	—	10	—	—
trans-1,4-Dimethylcyclohexane	C_8H_{16}	—	16	—	—
1-Octene	C_8H_{16}	—	8	—	—
2-Octene	C_8H_{16}	—	14	—	—
2,3,4-Trimethyl-1-pentene	C_8H_{16}	—	5	—	—
2,4,4-Trimethyl-1-pentene	C_8H_{16}	—	−29	—	—
2,3,4-Trimethyl-2-pentene	C_8H_{16}	—	1	—	—
2,4,4-Trimethyl-2-pentene	C_8H_{16}	—	2	—	—
3,4,4-Trimethyl-2-pentene	C_8H_{16}	—	< 21	—	—
2-Ethylhexanal	$C_8H_{16}O$	—	—	—	197
2,3-Dimethylhexane	C_8H_{18}	—	7(o)	—	—
2,4-Dimethylhexane	C_8H_{18}	—	10(o)	—	—
3-Ethyl-2-methylpentane	C_8H_{18}	—	< 21	—	—
2-Methylheptane	C_8H_{18}	—	4	—	—
3-Methylheptane	C_8H_{18}	—	−23	—	—
Octane	C_8H_{18}	—	13	1.0–4.7	220
2,2,3-Trimethylpentane	C_8H_{18}	—	< 21	—	—
2,2,4-Trimethylpentane	C_8H_{18}	—	−12	1.1–6.0	—
2,3,3-Trimethylpentane	C_8H_{18}	—	< 21	—	—
2,3,4-Trimethylpentane	C_8H_{18}	—	4	—	—
Dibutyl ether	$C_8H_{18}O$	—	25	1.5–7.6	194
Di-*tert*-butyl peroxide	$C_8H_{18}O_2$	—	12	—	—
Bis(2-ethoxyethyl) ether	$C_8H_{18}O_3$	—	—	—	205
2-(2-Butoxyethoxy)ethanol	$C_8H_{18}O_3$	—	—	—	225
Di-2-butylamine	$C_8H_{19}N$	—	24	—	—
Diisobutylamine	$C_8H_{19}N$	—	21	—	—
2,6-Dimethyl-3-heptene	C_9H_{18}	—	21(o)	—	—

Name	Formula	B.P./°C	Fl.P./°C	E.L./%	A.I.T./°C
1,3,5-Trimethylcyclohexane	C_9H_{18}	—	19	—	—
3,3-Diethylpentane	C_9H_{20}	—	< 21	0.7–7.7	—
2,5-Dimethylheptane	C_9H_{20}	—	23	—	—
3,5-Dimethylheptane	C_9H_{20}	—	23	—	—
4,4-Dimethylheptane	C_9H_{20}	—	21	—	—
3-Ethyl-2,3-dimethylpentane	C_9H_{20}	—	8	—	—
3-Ethyl-4-methylhexane	C_9H_{20}	—	24	—	—
4-Ethyl-2-methylhexane	C_9H_{20}	—	< 21	—	—
2- or 3-Methyloctane	C_9H_{20}	—	—	—	220
4-Methyloctane	C_9H_{20}	—	—	—	225
66Nonane	C_9H_{20}	—	—	—	205
2,2,5-Trimethylhexane	C_9H_{20}	—	13	—	—
2,2,3,3-Tetramethylpentane	C_9H_{20}	—	< 21	0.8–4.9	—
2,2,3,4-Tetramethylpentane	C_9H_{20}	—	< 21	—	—
Dicyclopentadiene	$C_{10}H_{12}$	—	−7(o)	—	—
2-Ethylhexyl vinyl ether	$C_{10}H_{20}O$	—	—	—	202
Isopentyl isovalerate	$C_{10}H_{20}O_2$	—	24	—	—
Decane	$C_{10}H_{22}$	—	—	—	210
2-Methylnonane	$C_{10}H_{22}$	—	—	—	210
Dipentyl ether	$C_{10}H_{22}O$	—	—	—	170
tert-Butyl peroxybenzoate	$C_{11}H_{14}O_3$	—	19	—	—
Dihexyl ether	$C_{12}H_{26}O$	—	—	—	185
Triisobutylaluminium	$C_{12}H_{27}Al$	—	< 0	—	< 4
Tributylphosphine	$C_{12}H_{27}P$	—	—	—	200
Tetradecane	$C_{14}H_{20}$	—	—	—	200
Hexadecane	$C_{16}H_{34}$	—	—	—	205
Dichlorosilane	$C_{12}H_2Si$	8.3	—	—	58±5°
Trichlorosilane	$C_{13}HSi$	32	−50	—	104
Deuterium	D_2	−249	—	5–75	—
Trifluorosilane	F_3HSi	−95	—	flammable	—
Tetrafluorohydrazine	F_4N_2	−73	—	—	explosive
Germane	GeH_4	−90	—	—	ambient
Digermane	Ge_2H_6	29	—	—	—
Hydrogen	H_2	−253	—	4.1–74.2	—
Hydrogen sulfide	H_2S	−62	—	4–44	—
Hydrogen disulfide	H_2S_2	—	< 22	—	—
Hydrogen selenide	H_2Se	−42	—	—	—
Hydrogen telluride	H_2Te	−2	—	—	−50°
Ammonia	H_3N	−33	—	15.8–25	—
Phosphine	H_3P	−88	—	1.79–?	see text
Stibine	H_3Sb	−17	—	—	—
Hydrazine	H_4N_2	—	38	4.7–100	23 on rust 132 on iron 156 on st. steel
Diphosphane	H_4P_2	—	—	—	ambient
Silane	H_4Si	−112	1.37–?	—	ambient
Disilane	H_6Si_2	−14.5	—	—	ambient
Trisilane	H_8Si_3	< 0	< 0	—	ambient
Phosphorus (white)	P	—	—	—	38.5
Sulfur (hot solid)	S	—	see text	see text	see text
Sulfur (hot liquid)	S	—	see text	—	see text

BOND GROUPINGS	*as in*	*CLASS ENTRIES*
$C\equiv C$		ACETYLENIC COMPOUNDS
$R_2C{=}N{=}N$		DIAZO COMPOUNDS; DIAZIRINES
$C\text{-}N^+{\equiv}N$		DIAZONIUM SALTS
N-O		*N-O* COMPOUNDS
$C\text{-}N{=}O$		NITROSO COMPOUNDS
$C\text{-}NO_2$		NITROALKANES; *C*-NITRO, POLYNITROALKYL and POLYNITROARYL COMPOUNDS
$C\text{-}O\text{-}N{=}O$		ACYL and ALKYL NITRITES
$C\text{-}O\text{-}\ NO_2$		ACYL AND ALKYL NITRATES
$C{=}N\text{-}O\text{-}$Metal		METAL FULMINATES; *aci*-NITRO COMPOUNDS
N-Metal		*N*-METAL DERIVATIVES
$Hg{=}N^+{=}Hg$		POLY(DIMERCURYIMMONIUM SALTS)
$N\text{-}N{=}O$		*N*-NITRO COMPOUNDS; NITROSO COMPOUNDS
$C\text{-}N{=}N\text{-}C$		AZO COMPOUNDS
$C\text{-}N{=}N\text{-}O\text{-}$		ARENEDIAZOATES; BIS(ARENEDIAZO) OXIDES
$N{\equiv}N^+\text{-}Ar\text{-}O^-$		ARENEDIAZONIUM OXIDES
$C\text{-}N{=}N\text{-}S\text{-}$		ARENEDIAZODIAZO SULFIDES; DIAZONIUM SULFIDES AND DERIVATIVES; THIATRIAZOLES
$C\text{-}N{=}N\text{-}N\text{-}C$		TRIAZENES
$\text{-}N_3$		AZIDES
$\text{-}N{=}N\text{-}N{=}N\text{-}$		TETRAZOLES; HIGH-NITROGEN COMPOUNDS
-O-O-		ORGANIC, INORGANIC and ORGANOMETALLIC PEROXIDES
$HN^+\ \ ^-OY$		OXOSALTS OF NITROGENOUS BASES; HYDRAZINIUM SALTS
$N^+\text{-}OH$		HYDROXYLAMINIUM SALTS
N-Hal		*N*-HALOGEN COMPOUNDS
O-Hal		PERCHLORATES; CHLORITE SALTS; HYPOHALITES; HALOGEN OXIDES
Three membered rings		AZIRIDINES; DIAZIRINES, 1,2-EPOXIDES; DIOXIRANES; CYCLOPROPANES

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Appendix 3

Glossary of Abbreviations and Technical Terms

ABS	A plastic which is a copolymer of acrylonitrile, butadiene and styrene
Aerobic	In presence of air
AIT	Autoignition temperature
Alloy	Mixture of 2 or more metals
Amalgam	Alloy of a metal with mercury
Ambient	Usual or surrounding
Anaerobic	In absence of air
Analogue	Compound of the same structural type
AO	Active oxygen content of peroxides
Aprotic	Without labile hydrogen atom(s)
Aqua regia	Mixture of nitric and hydrochloric acids
ARC	Accelerating rate calorimetry
ASTM	American Society for Testing and Materials
Autocatalytic	A reaction catalysed by its own products or intermediates, thus Self Accelerating
Autoxidation	Slow reaction with air
BAM	Bundes Anstalt für Materialsprüfung (similar to ASTM)
Basic	Fundamental, or, alkaline (acting as a base)
BLEVE	Boiling liquid expanding vapour explosion
Blowing agent	Material producing much gas on decomposition
b.p.	Boiling point
BSC	Bench scale calorimeter
Carbonaceous	Containing elemental carbon (as opposed to organic, containing combined carbon)
CHETAH	A computer program to predict energy release hazards
CIT	Critical ignition temperature
Class	Collection of related chemical groups or topics
COI	Critical oxygen index
conc.	concentrated
Congener	Compound with related but not identical structure
COT	Cyclooctatetraene

Cp	Cyclopentadienyl
Critical diameter	Minimum diameter of an explosive charge capable of maintaining detonation
Cryogenic	At a very low (freezing) temperature
CVD	Chemical vapour deposition
Deflagration	Self sustaining internal combustion propagating by means of molecular heat transfer slower than the speed of sound (the explosion mechanism of gunpowder and other ‘low’ explosives)
ΔH°_f	Standard heat of formation
Desiccate	Dry intensively
Detonable	Capable of detonation
Detonation	A self sustaining decomposition reaction propagating faster than the speed of sound by means of a shock wave (the characteristic property of ‘high’ as opposed to ‘low’ explosives).
Diglyme	Diethyleneglycol dimethyl ether
Digol	Diethyleneglycol
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EL	Explosive limits (or Flammable limits), vol% in air
Endotherm	Absorption of heat
ESCA	Electron scanning chemical analysis
Exotherm.	Liberation of (reaction) heat
Freeze drying	Drying without heat by vacuum evaporation of frozen solvent
GLC	Gas-liquid chromatography
Glyme	Ethyleneglycol dimethyl ether
Halocarbon	Partially or fully halogenated hydrocarbon
HMPA	Hexamethylphosphoramide
HMSO	Her Majesty’s Stationery Office
Homologue	Compound of the same (organic) series
Hypergolic	Ignites on contact
Ignition source	A source of energy which ignites flammables
IMS	Industrial methylated spirit (ethanol)
Induction period	Delay in reaction starting, caused by inhibitors
Inorganic	Not containing combined carbon, of mineral origin
Intermolecular	Between different molecules
Intramolecular	Within the same molecule
IR	Infrared spectroscopy
Initiation	Triggering of explosion or decomposition
LAH	Lithium tetrahydroaluminate
Lanthanide	Of the group of rare-earth metals
LRS	Laser Raman spectroscopy

LPG	Liquefied petroleum gas
MAPP	Methylacetylene/propadiene/propene mixture
Molecular sieve	A zeolite lattice with micropores of specific sizes, useful for molecular separations
m.p.	Melting point
MRH	Maximum reaction heat
NMR	Nuclear magnetic resonance spectrosopy
Nomenclature	System of naming chemicals
Off-spec.	Off-specification (low quality)
Oleum	Sulfur trioxide dissolved in sulfuric acid
Organic	A compound containing combined carbon
Organometallic	Containing carbon to metal bonding
Oxidant	Oxidising agent (electron sink)
PCB	Polychlorinated biphenyl
PTFE	Polytetrafluoroethylene
Propagation	Spread or transmission of decomposition, flame or explosion
Propellant	Energetic composition used in ballistics
PVC	Polyvinyl chloride
Pyrophoric	Igniting on contact with air (or frictional sparking)
Q	Heat of (exothermic) reaction or polymerisation
Quaternary salt	Tetra-substituted ammonium salt etc.
RCHD	Reactive Chemical Hazards Database, which you are using, either in book form or electronically
Redox	Reaction or Compound with reducing and oxidising features
Reducant	Reducing agent (electron source)
Refractory	Heat resisting
REITP2	A computer program to calculate MRH
RSC	Reaction Safety Calorimeter, or Royal Society of Chemistry
Runaway	Reaction out of control
Self-accelerating	Reaction catalysed by its own products
Self-heating	When substance generates heat faster than it is dissipated
Silicones	Organic derivatives of a polysiloxane chain
Slurry	Pourable mixture of solid and liquid
Smelt	Molten sodium sulfide and carbonate from evaporated sulfite liquor
Substance	Not a single chemical species, often of natural origin
Superheated	A liquid at a temperature above its boiling point
Tait24	Temperature of adiabatic storage which gives an induction time to exothermic decomposition of 24 hours
Thermite reaction	Reaction of aluminium powder and iron oxide producing molten iron (and analoguous reactions)
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
Thermochemistry	Study of heat effects of chemical reactions
TLC	Thin layer chromatography

TNT	Trinitrotoluene
U	Heat of (exothermic) decomposition
Unit operation	A single operational stage of a chemical process sequence – may be purely physical, e.g. distillation or drying
Unit process	A single chemical reaction stage in a process sequence
USNTIS	US National Technical Information Service
UV	Ultraviolet spectroscopy

Appendix 4

Index of Chemical Names and Synonyms used in Section 1

The majority of the names for chemicals in this alphabetically arranged index conform to one of the systematic series permitted under various sections of the IUPAC Definitive Rules for Nomenclature. Where there is a marked difference between these names and the alternative names recommended in the IUPAC-based BS2472:1983 or ASE 1985 nomenclature lists, or long established traditional names, these are given as synonyms in parentheses after the main title. These synonyms also have their own index entry, cross-referenced back to the IUPAC-based names used as bold titles in the text of Volume 1.

Those titles prefixed in the text with a dagger to show high flammability risks are prefixed similarly in this index. The four character numbers following the names or synonyms are the serial numbers of the entries, not page numbers.

It should be noted that italicised hyphenated prefixes which indicate structure, such as *cis*-, *o*-, *m*-, *tert*-, *mixo*-, *N*-, *O*-, etc., have been ignored during the alpha-sorting routine used on this index and the group-lists, while the roman character structural prefixes iso and neo, and roman multiplying prefixes such as di, tris, tetra and hexakis, have been included in the indexing procedure.

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Appendix 5

Index of CAS Registry Numbers *vs* Serial Numbers in Section 1

The CAS Registry numbers are the key to the full structural and stereochemical information held within the CAS chemical identification system, available both in printed form and on-line via several hosts worldwide.

The Index is arranged in numerically increasing order of the registry numbers. The serial numbers of those compounds for which no registry number has been found are listed separately at the end of the Index.

Serial numbers with no Registry number

0016
0017
0018
0024
0027
0034
0036
0037
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0040
0041
0042
0043
0044
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0237
0253
0263b
0267
0271
0289
0296
0303
0333
0337b
0366
0421
0427
0442
0470
0494b
0501
0513
0524
0532
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0568
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0610
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0664
0665
0670
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0707
0708b
0709
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0999
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1746
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2583c
2599
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2629b
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2680
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2800
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2804b
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2836b
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3065b
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3689b
3693
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3705a
3707
3711b
3712
3725
3727a
3731a
3733b
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3742
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3757
3759
3761b
3769
3773
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3808a
3813
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3870b
3880a
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4593a, b
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4648
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4662
4678
4680b
4697
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4733
4735
4736
4737
4756
4759
4763b
4766
4772
4775
4781
4786
4789
4853
4875

How to use the Handbook

To seek

1. **Stability data on single specific compounds:** look in Volume 1 using either the chemical name index (Appendix 4, Volume 1) or the empirical molecular formula at right of second title line (Carbon; then Hydrogen if present; other elements follow alphabetically) to locate the page. Membership of a general group is shown by a *See other*... cross-reference.
2. **Data on possible violent interaction between two or more compounds:** determine which appears "more reactive" and find it as in 1 above. Then look down the subentry titles for the other compound(s) involved which may be given as a single compound or as one of a group The latter are listed in Appendices 3 and 4 in Volume 2.
3. **General data on a class or group of compounds, or information on identity of individuals in a known hazardous group:** refer to the Alphabetical Volume 2. There is an alphabetical index to this Volume in Appendix 3, and a classified index in Appendix 4.
4. **Structure associated with explosive instability**: *See* EXPLOSIBILITY
5. **Information on general topics:** use the indexes in Appendix 3 or 4 in Volume 2.
6. **Fire-related data:** this is tabulated in Appendix 2, Volume 1.
7. **Information on a compound identified by its CAS Registry number:** there is a numerical index of CAS numbers *vs* Serial numbers in Appendix 5, Volume 1.

Do not assume that lack of information means that no hazard exists. Look further at related structures, using Appendix 3 or 4, Volume 2.

See rear end paper for **What the handbook provides.**

Readers are encouraged to submit details of new reactive hazards for inclusion in later editions. There is a page you can copy for this purpose at the end of both volumes.

What the Handbook Provides

In Volume 1 information on individual chemicals and the class or group(s) to which each belongs.

⑦ **0056. Aluminium tetrahydroborate (Aluminum borohydride)** ⑯

⑮ **[16962-07-5]** **AlB_3H_{12}** ①

$Al[BH_4]_3$ ②

⑭ 1. Schlessinger, H. I. *et al., J. Amer. Chem. Soc.*, 1940, **62**, 3421
2. Badin, F. J. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 2950

The vapour is spontaneously flammable in air [1], and explodes in oxygen, but only in presence of traces of moisture [2]. ⑥

⑪ Alkenes, Oxygen

Gaylord, 1956, 26
The tetrahydroborate reacts with alkenes and, in presence of oxygen, combustion is initiated even in absence of moisture. Butane explodes after an induction period while butadiene explodes immediately. ⑬

See other INDUCTION PERIOD INCIDENTS

Water MRH 1.72/36 ③

Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 4
Interaction at ambient temperature is explosive.

See other COMPLEX HYDRIDES ④

⑫ **†0596. Tetrafluoroethylene**

[116-14-3] **C_2F_4**

$F_2C{=}CF_2$

KEY:

1. Empirical formula which determines order in text
2. Structural formula
3. Calculated value for maximum reaction heat from the mixture
4. Cross reference to class entry in Volume 2
5. General class or group formula
6. Brief information on the class hazard
7. Full entry in Volume 1, Serial No 0056 is reproduced above
8. Cross reference to a related class
9. List of chemicals and serial numbers in Volume 1 which belong to this class

In Volume 2, information on classes of group of chemicals with similar structures or hazardous properties with lists of the individual chemicals comprising the class or group.

④ **COMPLEX HYDRIDES** **$[MH_n]^-, [EH_n]^-$** ⑤

1. Gaylord, 1956
2. Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 1–13
3. Ashby, E. C., *Rept. AD-A057764*, Richmond (Va.), USNTIS, 1978

This class of highly reactive compound includes several which have found extensive use in preparative chemistry [1]. Properties and reactions of several covalent tetrahydroborates have been reviewed [2]. Preparation and properties of several new hydrides are given which are of interest as high-energy fuels in propellant systems [3]. Individually indexed compounds are: ⑩

* Aluminium dichloride hydride diethyl etherate, 0061
Aluminium tetrahydroborate, 0058
Caesium hexahydroaluminate(3—), 0067
Copper tetrahydroaluminate, 0068
Lithium tetrahydroaluminate, 0075 ⑨
Lithium tetrahydroborate, 0145
Manganese(II) tetrahydrolaluminate, 0086
Potassium hexahydroaluminate, 0077
Sodium tetrahydroaluminate, 0076

See other REDUCANTS *See also* METAL HYDRIDES, NON-METAL HYDRIDES

⑧

* *denotes a chemical with a structure related to that of the class or group. See front end-paper for* **How to use the handbook.**

10. Literature reference to general class hazards. Textbooks (no initials) listed in Appendix 1 (both Volumes)

11. Chemical class or group title, ordered alphabetically, listed in Appendix 3 and classified in Appendix 4 (Volume 2)

12. †The material is of high fire potential, properties tabulated in Appendix 2 (Volume 1)

13. Reference(s) and hazards with other chemicals

14. Reference(s) and hazards of the title material

15. CAS Registry Number. Index in Appendix 5 (Volume 1)

16. Serial no., chemical name and synonym. Index in Appendix 4 (Volume 1)

AN INDEXED GUIDE TO PUBLISHED DATA

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Seventh Edition — Volume 2

Edited by
P G Urben

Assisted by
M J Pitt
Department of Chemical and Process Engineering
University of Sheffield

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INTRODUCTION

REACTIVE CHEMICAL HAZARDS

CLASS, GROUP AND TOPIC

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Introduction

THIS SHOULD BE READ THROUGH CAREFULLY
TO GAIN FULL BENEFIT FROM WHAT FOLLOWS

Aims of the Handbook

This compilation has been prepared and revised to give access to a wide and up-to-date selection of documented information to research students, practising chemists, safety officers and others concerned with the safe handling and use of reactive chemicals. This will allow ready assessment of the likely potential for reaction hazards which may be associated with an existing or proposed chemical compound or reaction system.

A secondary, longer-term purpose is to present the information in a way which will, as far as possible, bring out the causes of, and interrelationships between, apparently disconnected facts and incidents. This is designed to encourage an increased awareness of potential chemical reactivity hazards in school, college and university teaching laboratories, and to help to dispel the relative ignorance of such matters which is still in evidence in this important area of safety training during the formative years of technical education.

Others involved in a more general way with the storage, handling, packing, transport and distribution of chemicals, or emergencies related thereto, are likely to find information of relevance to their activities.

Scope and source coverage

This Handbook includes all information which had become available to the Editor by the end of 2004 on the reactivity hazards of individual elements or compounds, either alone or in combination. Appropriate source references are included to give access to more expansive information than that compressed into the necessarily abbreviated text entries.

A wide variety of possible sources of published information has been scanned to ensure maximum coverage. Primary sources have largely been restricted to journals known to favour or specialise in publication of safety matters, and the textbook series specialising in synthetic and preparative procedures.

Secondary sources have been a fairly wide variety of both specialised and general textbooks and encyclopaedic collections (notably those of Mellor, Sidgwick, Pascal and Bailar in the inorganic area, Houben-Weyl in the organic and organometallic areas, and both Kirk-Othmer and Ullmann in the industrial area). Section 50 of *Chemical Abstracts*, the CAS selection *Chemical Hazards, Health, & Safety*, the *Universities' Safety Association Safety News* (now lapsed), the CIA *CISHC Chemical Safety Summary*, (publication of which ceased in 1986 after 56 years), and the IChemE *Loss Prevention Bulletin* have been rich sources, together with the later recent RSC *Laboratory Hazards Bulletin* and *Chemical Hazards in Industry*. Additionally, various safety manuals, compilations, summaries, data sheets and case histories have been used, and fuller details of the sources used are set out in Appendix 1. References in the text to textbooks listed in Appendix 1 are characterised by absence of the author's initials after the surname.

Data taken from the Internet has been included when it fulfills two of the following three criteria: The Editor finds it credible; the source is authoritative; the hazard or incident was not previously included.

Information on toxic hazards has been specifically excluded because it is available elsewhere in many well-ordered and readily usable forms. However it should be remembered that many of the compounds included in this Handbook show high reactivity of one sort or another toward other materials, so may in general terms be expected to be reactive even in brief contact with animal organisms or tissue (including yours), with possible toxic effects, either acute or chronic. Toxicity has, however, been considered when a chemical reaction not forseeable by the average student generates a volatile poison – there is no warning that sulfides and acids generate hydrogen sulfide, frequent cause of fatality though that is, but generation of carbon monoxide by interaction of alkali and dried milk is covered.

No attempt has been made to include details of all flammable or combustible materials capable of burning explosively when mixed with air and ignited, nor of most incidents related to this most frequent cause of accidents, such information again being available elsewhere. However, to focus attention on the potential hazards always associated with the use of flammable and especially highly flammable substances, some 560 gases and liquids with flash points below 25°C and/or autoignition temperature below 225°C have been included in the text, their names prefixed with a dagger. The numerical values of the fire hazard-related properties of flash point, autoignition temperature and explosive (flammability) limits in air where known are given in the tabular Appendix 2. Those elements or compounds which ignite on exposure to air are included in the text, but not in the Table.

General arrangement

The information presented on reactive hazards is of two main types, specific or general, and these types of information have been arranged differently in their respective separate volumes 1 and 2.

Specific information on instability of individual chemical compounds, and on hazardous interactions of elements and/or compounds, is contained in the main formula-based Volume 1 of the Handbook. For an example of an unstable compound, *see* Ethyl perchlorate, p. 361
For an example of a hazardous interaction between 2 compounds,
see Nitric acid: Acetone, p. 1635

or 2 separate examples involving the same compound,
see Nitric acid: Acetone, or: Ethanol, pp. 1635, 1636
and one involving 3 compounds,
see Hydrogen peroxide: Nitric acid, Thiourea, p. 84

General information relating to classes or groups of elements or compounds possessing similar structural or hazardous characteristics is contained in the smaller alphabetically based Volume 2.

See ACYL NITRATES, p. 10
PYROPHORIC METALS, p. 354

References in the text to these general classes or groups of materials is always in small capitals to differentiate them from references to specific chemicals, the names of which are given in normal roman typeface.

Some individual materials of variable composition (substances) and materials which cannot conveniently be formulated and placed in Volume 1 are also included in this general section.

See BLEACHING POWDER, CELLULOSE NITRATE, pp. 57, 66

Both theoretical and practical hazard topics, some indirectly related to the main theme of this book, are also included.

See DISPOSAL, EXPLOSIBILITY, pp. 110, 131
GAS CYLINDERS, OXYGEN ENRICHMENT, pp. 150, 307

Several topics which bring together incidents involving a common physical cause or effect but different types of chemicals are now included in Volume 2.

See CATALYTIC IMPURITY INCIDENTS, p. 63
GAS EVOLUTION INCIDENTS, p. 150

Specific chemical entries (Volume 1)

A single unstable compound of known composition is placed in the main first volume and is located on the basis of its empirical molecular formula expressed in the Hill system used by *Chemical Abstracts* (C and H if present, then all other element symbols alphabetically). The use of this indexing basis permits a compound to be located if its structure can be drawn, irrespective of whether a valid name is known for it. A representation of the structure of each compound is given on the third bold title line while the name of the compound appears as the first bold title line. References to the information source are given, followed by a statement of the observed hazard, with any relevant explanation. Cross-reference to similar compounds, often in a group entry, completes the entry. *See* Trifluoroacetyl nitrite, p. 270

Where two or more elements or compounds are involved in a reactive hazard, and an intermediate or product of reaction is identifiable as being responsible for the hazard, both reacting substances are normally cross-referred to the identified product. The well-known reaction of ammonia and iodine to give explosive nitrogen triodide-ammonia is an example of this type. The two entries

Ammonia: Halogens, p. 1730
Iodine: Ammonia, p. 1794

are referred back to the main entry under the identified material

Nitrogen triiodide-ammonia, p. 1799

No attempt has been made, however, to list all combinations of reactants which can lead to the formation of a particular main entry compound.

In a multi-reactant system where no identification of an unstable product was possible, one of the reactants had to be selected as primary reactant to prepare and index the main entry, with the other material(s) as secondary reactant(s). No strictly logical basis of choice for this is obvious.

However, it emerged during the compilation phase that most two component reaction hazard systems of this type involve a fairly obvious oxidant material as one of the reactants. Where this situation was recognised, the oxidant has normally been selected as primary (indexing) reactant, with the other as secondary reactant, following the colon.

See Potassium permanganate: Acetic acid, etc., p.1811

In the markedly fewer cases where an obvious reducant has been involved as one reactant, that was normally selected as primary reactant.

See Lithium tetrahydroaluminate: 3,5-Dibromocyclopentene, p. 47

In the relatively few cases where neither (or none) of the reactants can be recognised as an oxidant or reducant, the choice was made which appeared to give the more informative main entry text.

See Chloroform: Acetone, etc., p. 163

Where some hazard has been noted during the preparation of a specific compound, but without it being possible to identify a specific cause, an entry for that compound states 'Preparative hazard', and back-refers to the reactants involved in the preparation.

See Sulfur dioxide, p. 1948

Occasionally, departures from these considerations have been made where such action appeared advantageous in bringing out a relationship between formally unrelated compounds or hazards. In all multi-component cases, however, the secondary reactants (except air and water) appear as formula entries back-referred to the main entry text, so that the latter is accessible from either primary or secondary reactants.

See Dimethyl sulfoxide: Acyl halides (main entry), p. 381
Acetyl chloride: Dimethyl sulfoxide (back reference), p. 312

Grouping of reactants

There are advantages to be gained in grouping together elements or compounds showing similar structure or reactivity, because this tends to bring out the relationships between structure and activity more clearly than separate treatment. This course has been adopted widely for primary reactants (see next heading), and for secondary reactants where one primary reactant has been involved separately with a large number of secondary materials. Where possible, the latter have been collected together under a suitable general group title indicative of the composition or characteristics of those materials.

See Chlorine: Hydrocarbons, p. 1452
Hydrogen peroxide: Metals, Metal oxides, Metal salts, p. 1705
Hydrogen sulfide: Oxidants, p. 1722

This arrangement means, however, that some practice will be necessary on the user's part in deciding into what group an individual secondary reactant falls before the longer-term advantages of the groupings become apparent. The formal group titles listed in Appendix 5, and classified in Appendix 6, will be of use in this connection. However, it should be noted that sometimes informal group titles are used which do not appear in these Appendices.

General group entries (Volume 2)

In some cases literature references relating to well-defined groups of hazardous compounds or to hazard topics have been found, and these are given, with a condensed version of relevant information at the beginning of the topic or group entry, under a suitable bold title, the latter being arranged in alphabetical order in Volume 2.

Cross references to related group or sub-group entries are also included, with a group list of the names and serial (not page) numbers of the chemicals appearing in Volume 1 which lie within the structural or functional scope of the group entry title. Compounds which are closely similar to, but not in strict conformity with, the group definition are indicated by a prefixed asterisk.

The group entries thus serve as sub-indexes for each structurally based group of hazardous compounds. Conversely, each individual compound entry is back-referred to the group entry, and thence to all its strict structural analogues and related congeners included in Volume 1 of this Handbook. Note that these group lists of chemicals are now in alphabetical (not formula) order, and give the serial number (not page number) for the chemical.

These features should be useful in attempts to estimate the stability or reactivity of a compound or reaction system which does not appear in this Handbook. The effects on stability or reactivity of changes in the molecular structure to which the destabilising or reactive group(s) is attached are in some cases discussed in the group entry. Otherwise such information may be gained from comparison of the information available from the individual compound entries listed collectively (now in alphabetical order, with serial number) in the group entry.

Care is, however, necessary in extrapolating from the described properties of compounds to others in which the user of this Handbook may be interested. Due allowance must be made for changes in elemental reactivity up or down the columns of the Periodic Table, and for the effects of variation in chain length, branching and point of group-attachment in organic systems. Purity of materials, possible catalytic effects (positive or negative) of impurities, and scale of operations may all have a direct bearing upon a particular reaction rate. These and other related matters are dealt with in more detail in the following Introductory Chapter.

Nomenclature

With the direct encouragement and assistance of the Publishers, an attempt has been made to use chemical names which conform to recent recommendations of IUPAC. While this has not been an essential part of the compilation, because each title name has the corresponding structural and molecular formula adjacent, it seems nonetheless desirable to minimise possible confusion by adopting the unambiguous system of nomenclature presented in the IUPAC publications.

Where the IUPAC name for a compound is very different from a previously used recent trivial name, the latter is included as a synonym in parentheses (and in single quotes where no longer an acceptable name). Generally, retained trivial names have not been used as main entry titles, but they have often been included in the entry texts. Rarely, on the grounds of brevity, names not conforming strictly to IUPAC principles but recommended for chemicals used in industry in BS 2474: 1983 have been used. The prefix *mixo*-, to represent the mixtures of isomers sometimes used as industrial materials, is a case in point.

Some of the rigidly systematic names selected by the Association for Science Education for their nomenclature list in 1985 from the IUPAC possibilities, and some of the systematic indexing names used by *Chemical Abstracts* since 1972, are given as synonyms in the Index of Chemical Names. This should assist those coming into industry and research with a command of those nomenclature systems but who may be unfamiliar with the current variety of names used for chemicals. The inclusion, where possible, of the CAS Registry Number for each title compound should now simplify the clarification of any chemical name or synonym problems, by reference to the Registry Handbook or other CAS source.

In connection with the group titles adopted for the alphabetically ordered Volume 2, it has been necessary in some cases to devise group names (particularly in the inorganic field) to indicate in a very general way the chemical structures involved in various classes, groups or sub-groups of compounds. For this purpose, all elements have been considered either as METALS or NON-METALS, and of the latter, HALOGENS, HYDROGEN, NITROGEN, OXYGEN, and SULFUR were selected as specially important. Group names have then been coined from suitable combinations of these, such as the simple

METAL OXIDES, NON-METAL SULFIDES
N-HALOGEN COMPOUNDS, NON-METAL HYDRIDES
METAL NON-METALLIDES, COMPLEX HYDRIDES

or the more complex

METAL OXOHALOGENATES
AMMINECHROMIUM PEROXOCOMPLEXES
OXOSALTS OF NITROGENOUS BASES
METAL OXONON-METALLATES

Organic group entries are fairly conventional, such as

HALOALKENES
NITROARL COMPOUNDS
DIAZONIUM SALTS

Where necessary, such group names are explained in the appropriate group entry, of which a full listing is given in Appendix 5, and a classified listing in Appendix 6.

Cross reference system

The cross-reference system adopted in this Handbook plays a large part in providing maximum access to, and use of, the rather heterogeneous collection of information

herein. The significance of the five types of cross-reference which have been used is as follows.
See ... refers to a directly related item.
See also ... refers to an indirectly related item.
See other ... refers to listed strict analogues of the compound etc.
See related ... refers to listed related compounds (congeners) or groups not strictly analogous structurally.
See entry ... points to a or the relevant reference in Volume 2.
CROSS REFERENCES IN CAPITALS REFER TO VOLUME 2

Information content of individual entries

A conscious effort has been made throughout this compilation to exclude much fringe information not directly relevant to the involvement of chemical reactivity in the various incidents or observations, while giving enough detail to allow the reader to judge the relevance or otherwise of the quoted reference(s) to his or her particular reactivity problems or interests.

It must be stressed that this book can do no more than to serve as a guide to much more detailed information available *via* the quoted references. In all but a few cases it cannot relieve the student or chemist of their moral and now legal obligation to themselves and to their co-workers, to equip themselves with the fullest possible information from the technical literature resources which are widely available, *before* attempting any experimental work with materials known, or suspected, to be hazardous or potentially so. It could be impossible for you *after* the event.

THE ABSENCE OF A MATERIAL OR A COMBINATION OF MATERIALS FROM THIS HANDBOOK CANNOT BE TAKEN TO IMPLY THAT NO HAZARD EXISTS. LOOK THEN FOR ANALOGOUS MATERIALS USING THE GROUP ENTRY SYSTEM AND THE INDEXES THERETO.

One aspect which, although it is absent from most entry texts, is nevertheless of vital importance, is that of the potential for damage, injury or death associated with the various materials and reaction systems dealt with in this Handbook.

Though some of the incidents have involved little or no damage (*see* CAN OF BEANS, p. 61), others have involved personal injuries, often of unexpected severity (*see* SODIUM PRESS, p. 380), and material damage is often immense. For example, the incident given under Perchloric acid: Cellulose derivatives, (reference 1, p. 65) involved damage to 116 buildings and a loss approaching 3M dollars at 1947 values. The death-roll associated with reactive chemical hazards has ranged from 1 or 2 (*see* Tetrafluoroethylene: Iodine pentafluoride, p. 1601) to some 600 with 2000 injured in the incident at Oppau in 1921 (*see* Ammonium nitrate, reference 4, p. 1749), and now to several thopusand, with more than 100,000 injured, by methyl isocyanate fumes at Bhopal in 1984 (reference 7, p. 288).

This sometimes vast potential for destruction again emphasises the need to gain the maximum of detailed knowledge *before* starting to use an unfamiliar chemical or reaction system.

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Reactive Chemical Hazards

This introductory chapter seeks to present an overview of the complex subject of reactive chemical hazards, drawing attention to the underlying principles and to some practical aspects of minimising such hazards. It also serves in some measure to correlate some of the topic entries in the alphabetically arranged Section 2 of the Handbook.

Basics

All chemical reactions implicitly involve energy changes (energy of activation + energy of reaction), for these are the driving force. The majority of reactions liberate energy as heat (occasionally as light or sound) and are termed exothermic. In a minority of reactions, the reaction energy is absorbed into the products, when both the reaction and its products are described as endothermic.

All reactive hazards involve the release of energy in quantities or at rates too high to be absorbed by the immediate environment of the reacting system, and material damage results. The source of the energy may be an exothermic multi-component reaction, or the exothermic decomposition of a single unstable (often endothermic) compound.

All measures to minimise the possibility of occurrence of reactive chemical hazards are therefore directed at controlling the extent and rate of release of energy in a reacting system. In an industrial context, such measures are central to modern chemical engineering practice. Some of the factors which contribute to the possibility of excessive energy release, and appropriate means for their control, are now outlined briefly, with references to examples in the text.

Kinetic factors

The rate of an exothermic chemical reaction determines the rate of energy release, so factors which affect reaction kinetics are important in relation to possible reaction hazards. The effects of proportions and concentrations of reactants upon reaction rate are governed by the Law of Mass Action, and there are many examples where changes in proportion and/or concentration of reagents have transformed an established uneventful procedure into a violent incident. For examples of the effect of increase in proportion,

see 2-Chloronitrobenzene: Ammonia
Sodium 4-nitrophenoxide

For the effect of increase in concentration upon reaction velocity,

see Dimethyl sulfate: Ammonia
Nitrobenzene: Alkali (reference 2)

The effects of catalysts (which effectively reduce the energy of activation), either intentional or unsuspected, is also relevant in this context. Increase in the concentration of a catalyst (normally used at 1-2%) may have a dramatic effect on reaction velocity.

See Trifluoromethanesulfonic acid: Acyl chlorides, etc
2-Nitroanisole: Hydrogen
HYDROGENATION CATALYSTS

The presence of an unsuspected contaminant or catalytic impurity may affect the velocity or change the course of reaction. For several examples,

see CATALYTIC IMPURITY INCIDENTS

In the same context, but in opposite sense, the presence of inhibitors (negative catalysts, increasing energy of activation) may seriously interfere with the smooth progress of a reaction. An inhibitor may initiate an induction period which can lead to problems in establishing and controlling a desired reaction. For further details and examples,

see INDUCTION PERIOD INCIDENTS

Undoubtedly the most important factor affecting reaction rates is that of temperature. It follows from the Arrhenius equation that the rate of reaction will increase exponentially with temperature. Practically, it is found that an increase of 10°C in reaction temperature often doubles or trebles the reaction velocity.

Because most reactions are exothermic, they will tend to accelerate as reaction proceeds unless the available cooling capacity is sufficient to prevent rise in temperature. Note that the exponential temperature effect accelerating the reaction will exceed the (usually) linear effect of falling reactant concentration in decelerating the reaction. When the exotherm is large and cooling capacity is inadequate, the resulting accelerating reaction may proceed to the point of loss of control (runaway), and decomposition, fire or explosion may ensue.

The great majority of incidents described in the text may be attributed to this primary cause of thermal runaway reactions. The scale of the damage produced is related directly to the size, and more particularly to the *rate*, of energy release.

See RUNAWAY REACTIONS

Reactions at high pressure may be exceptionally hazardous owing to the enhanced kinetic energy content of the system.

See HIGH-PRESSURE REACTION TECHNIQUES

Although detailed consideration of explosions is outside the scope of this Handbook, three levels of intensity of explosion (i.e. rates of fast energy release) can be discerned and roughly equated to the material damage potential.

Deflagration involves combustion of a material, usually in presence of air. In a normal liquid pool fire, combustion in an open situation will normally proceed without explosion. Mixtures of gases or vapours with air within the explosive limits which are subsequently ignited will burn at normal flame velocity (a few m/s) to produce a ‘soft’ explosion, with minor material damage, often limited to scorching by the moving flame front. Injuries to personnel may well be more severe.

If the mixture (or a dust cloud) is confined, even if only by surface irregularities or local partial obstructions, significant pressure effects can occur. Fuel-air mixtures near to stoicheiometric composition and closely confined will develop pressures of several bar within milliseconds, and material damage will be severe. Unconfined vapour explosions of large dimensions may involve higher flame velocities and significant pressure effects, as shown in the Flixborough disaster.

See DUST EXPLOSION INCIDENTS
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION
VAPOUR CLOUD EXPLOSIONS

Detonation is an extreme form of explosion where the propoagation velocity becomes supersonic in gaseous, liquid or solid states. The temperatures and particularly pressures associated with detonation are higher by orders of magnitude than in deflagration. Energy release occurs in a few microseconds and the resulting shattering effects are characteristic of detonation. Deflagration may accelerate to detonation if the burning material and geometry of confinement are appropriate (endothermic compounds, long narrow vessels or pipelines).

See Acetylene (reference 9)
ENDOTHERMIC COMPOUNDS
EXPLOSIONS
UNIT PROCESS INCIDENTS

Factors of importance in preventing such thermal runaway reactions are mainly related to the control of reaction velocity and temperature within suitable limits. These may involve such considerations as adequate heating and particularly cooling capacity in both liquid and vapour phases of a reaction system; proportions of reactants and rates of addition (allowing for an induction period); use of solvents as diluents and to reduce viscosity of the reaction medium; adequate agitation and mixing in the reactor; control of reaction or distillation pressure; use of an inert atmosphere.

See AGITATION INCIDENTS

In some cases it is important not to overcool a reaction system, so that the energy of activation is maintained.

See Acetylene: Halogens (reference 1)

Adiabatic Systems

Because process heating is expensive, lagging is invariably applied to heated process vessels to minimise heat loss, particularly during long-term hot storage. Such adiabatic or near-adiabatic systems are potentially hazardous if materials of limited thermal stability, or which possess self-heating capability, are used in them. Insufficiently stabilised bulk-stored monomers come into the latter category.

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent
POLYMERISATION INCIDENTS
SELF-HEATING AND IGNITION INCIDENTS
THERMAL STABILITY OF REACTION MIXTURES
VIOLENT POLYMERISATION

Reactivity vs. Composition and Structure

The ability to predict reactivity and stability of chemical compounds from their composition and structure is as yet limited, so the ability accurately to foresee potential hazards during preparation, handling and processing of chemicals and their mixtures is also restricted. Although some considerable progress has been made in the use of computer programs to predict hazards, the best available approach for many practical purposes appears to be an initial appraisal based on analogy with, or extrapolation from, data for existing compounds and processes. This preliminary assessment can be supplemented with calorimetric instrumental examination, then bench-scale testing procedures for thermal stability applied to realistic reaction mixtures and processing conditions, should any doubt of safety persist. A wide range of equipment and techniques is now available for this purpose.

See ACCELERATING RATE CALORIMETRY
ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
COMPUTATION OF REACTIVE CHEMICAL HAZARDS
DIFFERENTIAL SCANNING CALORIMETRY
DIFFERENTIAL THERMAL ANALYSIS
MAXIMUM REACTION HEAT
REACTION SAFETY CALORIMETRY

It has long been recognised that instability in single compounds, or high reactivity in combinations of different materials, is usually associated with particular groupings of atoms or other features of molecular structure, such as high proportions or local concentrations of oxygen or nitrogen. Details of such features associated with explosive instability are collected under the heading EXPLOSIBILITY.

An approximate indication of likely instability in a compound may be gained from inspection of the empirical molecular formula to establish stoicheiometry.

See HIGH-NITROGEN COMPOUNDS
OXYGEN BALANCE

Endothermic compounds, formed as the energy-rich products of endothermic reactions, are thermodynamically unstable and may be liable to energetic decomposition with low energy of activation.

See ENDOTHERMIC COMPOUNDS

Reaction Mixtures

So far as reactivity between different compounds is concerned, some subdivision can be made on the basis of the chemical types involved. Oxidants (electron sinks) are undoubtedly the most common chemical type to be involved in hazardous incidents, the other components functioning as fuels or other electron sources. Air (21% oxygen) is the most widely dispersed oxidant, and air-reactivity may lead to either short- or long-term hazards.

Where reactivity of a compound is very high, oxidation may proceed so fast in air that ignition occurs.

See PYROPHORIC MATERIALS

Slow reaction with air may lead to the longer-term hazard of peroxide formation.

See AUTOXIDATION
PEROXIDATION INCIDENTS
PEROXIDES IN SOLVENTS
PEROXIDISABLE COMPOUNDS

Oxidants more concentrated than air are of greater hazard potential, and the extent of involvement of the common oxidants

Perchloric acid
Chlorine
Nitric acid
Hydrogen peroxide
Sulfuric acid
METAL CHLORATES

may be judged from the large number of incidents in the text involving each of them, as well as other OXIDANTS.

At the practical level, experimental oxidation reactions should be conducted to maintain in the reacting system a minimum oxygen balance consistent with other processing requirements. This may involve adding the oxidant slowly with appropriate mixing and cooling to the other reaction materials to maintain the minimum effective concentration of oxidant for the particular reaction. It will be essential to determine by a suitable diagnostic procedure that the desired reaction has become established, to prevent build-up of unused oxidant and a possible approach to the oxygen balance point.

See OXYGEN BALANCE

Reducants (rich electron sources) in conjunction with reducible materials (electron acceptors) feature rather less frequently than oxidants in hazardous incidents.

See REDUCANTS

Interaction of potent oxidants and reducants is invariably highly energetic and of high hazard potential.

See Dibenzoyl peroxide: Lithium tetrahydroaluminate
Hydrazine: Oxidants
REDOX REACTIONS
ROCKET PROPELLANTS

Similar considerations apply to those compounds which contain both oxidising and reducing functions in the same molecular structure.

See REDOX COMPOUNDS

Water is, after air, one of the most common reagents likely to come into contact with reactive materials, and several classes of compounds will react violently, particularly with restricted amounts of water.

See WATER-REACTIVE COMPOUNDS

Most of the above has been written with deliberate processing conditions in mind, but it must be remembered that the same considerations will apply, and perhaps to a greater degree, under the uncontrolled reaction conditions prevailing when accidental contact of reactive chemicals occurs in storage or transit.

Adequate planning is therefore necessary in storage arrangements to segregate oxidants from fuels and reducants, and fuels and combustible materials from compressed gases and water-reactive compounds. This will minimise the possibility of accidental contact and violent reaction arising from faulty containers or handling operations, and will prevent intractable problems in the event of fire in the storage areas.

See SAFE STORAGE OF CHEMICALS

Unexpected sources of ignition may lead to ignition of flammable materials during chemical processing or handling operations.

See FRICTIONAL IGNITION OF GASES
IGNITION SOURCES
SELF-HEATING AND IGNITION INCIDENTS
STATIC INITIATION INCIDENTS

Protective Measures

The need to provide protective measures will be directly related to the level of potential hazards which may be assessed from the procedures outlined above. Measures concerned with reaction control are frequently mentioned in the following text, but details of techniques and equipment for personal protection, though usually excluded from the scope of this work, are obviously of great importance.

Careful attention to such detail is necessary as a second line of defence against the effects of reactive hazards. The level of protection considered necessary may range from the essential and absolute minimum of effective eye protection, *via* the safety screen, fume cupboard or enclosed reactor, up to the ultimate of a remotely controlled and blast-resistant isolation cell (usually for high-pressure operations). In the absence of facilities appropriate to the assessed level of hazard, operations must be deferred until such facilities are available.

Volume 2

Class, Group and Topic

(Entries arranged in alphabetical order)

EXPLANATORY NOTES

The entries in this volume are of two distinct types, each accounting for about half of the total of almost 700 entries. The first type of entry gives general information on the hazardous behaviour of some recognisably discrete classes or groups of the more than 5000 individual compounds for which details are given in Volume 1.

Where possible, a general structural formula ranged right on the title line indicates the typical structure(s) of the members of each class of group of compounds. In these formulae, the following general symbols are used in addition to the usual symbols for the elements.

Ar = AROMATIC nucleus

E = NON-METALLIC element

M = METALLIC element

R = organic RESIDUE

X = HALOGEN

Z = non-halogen ANION species

Information on the derivation of the class and group names is given in the Introduction.

The second type of entry concerns reactive hazard topics, techniques or incidents which have a common theme or pattern of behaviour involving compounds of several different groups, so that no common structural feature exists for the compounds involved.

The more than 300 group-lists of compounds in the first type of entry serve as an index to analogues and homologues of a compound falling within the scope of the structural or behavioural group. Those compounds (congeners) of generally similar, but not identical structure to the majority in the group-lists are prefixed *. Flammable analogues are prefixed † to remind of the fire hazard. For flammable congeners, the dagger prefix has taken precedence over the asterisk for the same reason. The order in the group-lists is alphabetic, rather than being order of empirical formulae as in the main text of Volume 1.

There is a full index to the the Volume 2 entry titles in Appendix 3. Appendix 4 contains the same entries classified on the basis of similarity in type of information content, as indicated by the bold sub-titles. This Appendix should be useful in locating reaction hazard information of a more general nature.

Details of corrections of typographical or factual errors, or of further items for inclusion in the text, will be welcomed, and a page which can be photocopied for this purpose will be found at the back of the book.

ABS

Kao, C-S. *et al., Proc. 33rd Annu. Loss Prev. Symp.*, 6d/1

A series of explosions in silos of an acrylonitrile/butadiene/styrene resin plant appears to have been a conventional dust explosion.

DUST EXPLOSION INCIDENTS (reference 22)

ABSORBENTS

Time was when chemical spillages were flushed to drain. Environmental concerns mean that they are now absorbed onto absorbents, then drummed up for later disposal. The absorbents are selected to be unreactive and usually warn of classes of chemicals with which they should not be used. They do not change the inherent properties of the spilt chemical, which can sometimes give rise to trouble when drummed up, especially since contaminants will also often be introduced. Drums for disposal should not be stored in occupied enclosed spaces and it is probably unwise that they be sealed.

See Phenyloxirane

See also INSULATION

ACCELERATING RATE CALORIMETRY (ARC)

1. Townsend, D. I. *et al., Thermochim. Acta*, 1980, **37**, 1—30
2. Townsend, D. I., *Runaway Reactions*, 1981, Paper 3Q, 1—14
3. Coates, C. F., *Chem. & Ind.*, 1984, 212—216
4. Gibson, N., *Chem. & Ind.*, 1984, 209—212
5. *Explosion at the Dow Chemical Factory, King's Lynn, 27th June 1976*, London, HSE, 1977
6. Cardillo, P. *et al., J. Haz. Mat.*, 1984, **9**, 221—234
7. Kikuchi, T., Sumitomo Kagaku (Osaka), 2001, (1), 62
8. Ralbovsky, P. J. *et al., Proc. of 29th NATAS Annual Conf. on Therm. Anal. & Appl.*, 2001, 543

Of the instrumental methods currently available for detailed small scale predictive investigation of hazardous and potentially hazardous reactions, the accelerating rate calorimeter appears to be the most sophisticated, sensitive, accurate and wide ranging in application. In essence the ARC maintains a sample in adiabatic condition once an exothermic reaction is detected, and then measures the consequent increases in temperature and pressure inside the sample holder in relation to elapsed time. The sample (1—5 g) is contained in a small spherical metal bomb, usable up to 500°C and 170 bar, within an insulated oven inside a massive steel containment vessel. The sample is heated on a stepped heat-wait-search programme until an exotherm is detected, when adiabatic conditions are then automatically established. The results can be processed to yield data relevant either to process control or reaction mechanism considerations. Fuller details of the theoretical background, construction and instrumentation, operation and capabilities of the technique have been published [1], and the theory behind the development of methods of estimating time to maximum rate of decomposition (TMR) from ARC results is discussed [2]. The place of ARC as part of a comprehensive hazard evaluation system in a chemical manufacturing context has been discussed [3]. The use of much simpler (and less expensive) Dewar flask methods for identifying potentially hazardous decompositions in reaction masses and powders has been compared and contrasted with ARC methods [4]. The part played by ARC in the investigation of the industrial explosions at King's Lynn (3,5-dinitro-2-toluamide) [5], and at Seveso (2,4,5-trichlorophenol) [6] shows the potential of the technique. Use of ARC to determine ADT_{24} (24 hour autodecomposition temperature) and 7 day self- accelerating decomposition temperature (SADT) to provide safe handling and storage temperatures is described [7]. An improved ARC system has been designed [8].

See ADIABATIC CALORIMETRY, CALORIMETRY, CHEMICAL STABILITY/REACTIVITY ASSESSMENT

ACCIDENTAL DECONTAMINATION

Kletz, T. A., *J. Loss Prev. Proc. Ind.*, 1989, **2**, 117

In a brief review of chemical accidents caused by accidental contamination of process materials, attention is drawn to the much less frequent opposite effect of accidental decontamination (or purification) as a cause of accidents. Some examples of the effects arising from accidental loss or inactivation of stabilisers or antioxidants from reactive materials are given.

See CATALYTIC IMPURITY INCIDENTS

ACCIDENT DATABASES

1. *The Accident Database*, Rugby, Institution of Chemical Engineers,
2. *MARS Database*, Ispra (Italy), Major Accident Hazards Bureau
3. *U.S. Chemical Safety and Hazard Investigation Board, Chemical Incident Reports Centre*, http://www.chemsafety.gov/circ
4. Uth, H-J. *et al., J. Haz. Mat.*, 2004, **111**(1-3), 139
5. Kletz, T. A. *et al., Chem. Eng. Progress*, 2001, **97**(10), 8

Several organisations have lately established electronic databases, recording details of industrial chemical accidents. These should enable the user to learn from others' mistakes and also establish a fixed version of accidents, which hitherto have changed in the retelling, and the more important have often been retold. The first two above are examples of a wider trend. All tend to reflect the pre-occupations of their compilers, which are generally not so much the precise chemical causes of the mishap, but its effects. A third, current reporting, database is of more universal scope, though its sources, including local newspapers and fire service reports, garble many of the reports [3]. Germany has assembled a database of major industrial accidents, not specifically chemical, from 1993 onwards, more recently supplemented by edited reported incidents, accessible via www.umweltbundesamt.de/zema/. Paper reports are also available [4]. A debate over safety databases, including incident ones, and their utility has appeared [5].

ACETYLENIC COMPOUNDS $C\equiv C$

1. Davidsohn, W. E. *et al., Chem. Rev.*, 1967, **67**, 74
2. Mushii, R. Ya. *et al., Chem. Abs.*, 1967, **67**, 92449
3. Dutton, G. G. S., *Chem. Age*, 1947, **56**(1436), 11—13
4. Kuwatani, Y. *et al., Chem. Abs.*, 1999, **131**, 170118k

The presence of the endothermic triply-bonded acetylene (ethyne) group confers explosive instability on a wide range of acetylenic compounds (notably when halogen is also present) and derivatives of metals (and especially of heavy metals) [1]. Explosive properties of butadiyne, buten-3-yne, hexatriyne, propyne and propadiene have been reviewed, with 74 references [2]. The tendency of higher acetylenes to explosive decomposition may be reduced by dilution with methanol [3]. A Japanese review of conjugated polyynes, including their explosibility, has been published [4]. The class includes the separately treated groups and the individually indexed compounds:

Acetylenedicarboxaldehyde, 1399
Acetylenedicarboxylic acid, 1401
Azido-2-butyne, 1469
3-Azidopropyne, 1111
Benzyloxyacetylene, 3127
Bis(cyclopentadienyl)hexafluoro-2-butynechromium, 3629
Bis(dibutylborino)acetylene, 3769
Bis(dipropylborino)acetylene, 3663
Butoxyacetylene, 2422
3-Butyn-1-yl 4-toluenesulfonate, 3393
2-Butyne-1,4-diol, 1523
2-Butyne-1-thiol, 1541
1-Chloro-3.phenylpent-1-en-4-yn-3-ol, 3387
N-Chloro-3-aminopropyne, 1126
* 3-Cyanopropyne, 1412
Di(1-propynyl) ether, 2319
Di(2-propynyl) ether, 2320
1,2-Di(3-buten-1-ynyl)cyclobutane, 3503
Dibutyl-3-methyl-3-buten-1-ynlborane, 3612
Diethyl acetylenedicarboxylate, 2982
1-Diethylamino-1-buten-3-yne, 3015
2,4-Diethynyl-5-methylphenol, 3387
cis-3,4-Diethynylcyclobut-3-ene-1,2-diol, 2916
2,4-Diethynylphenol, 3238
1,10-Di(methanesulfonyloxy)deca-4,6-diyne, 3537
Dimethyl acetylenedicarboxylate, 2333
3,3-Dimethyl-1-nitro-1-butyne, 2389
(Dimethylamino)acetylene, 1559
Diphenylethyne, 3627
4-Ethoxy-2-methyl-3-butyn-2-ol, 2840
1-Ethoxy-2-propyne, 1903
† Ethoxyacetylene, 1518
Ethynyl vinyl selenide, 1445
2-Ethynylfuran, 2205
2-Heptyn-1-ol, 2837
4,5-Hexadien-2-yn-1-ol, 2321
2,5-Hexadiyn-1-ol, 2322
1,5-Hexadiyn-3-one, 2206
2,4-Hexadiyne-1,6-dioic acid, 2087
2,4-Hexadiynylene chloroformate, 2885

2,4-Hexadiynylene chlorosulfite, 2155
Lithium ethynediolate, 0989
† Methoxyacetylene, 1143
3-Methoxypropyne, 1520
† Methyl propiolate, 1438
1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene, 3754
3-Methyl-2-penten-4-yn-1-ol, 2378
2-Methyl-3,5,7-octatriyn-2-ol, 3129
† 2-Methyl-3-butyn-2-ol, 1904
2-Nitrophenylpropiolic acid, 3107
2-Nonen-4,6,8-triyn-1-al, 3106
Octacarbondioxide pentamer, 3898
Octacarbondioxide tetramer, 3878
Octatetrayne-1,8-dicarboxylic acid, 3229
Oligo(octacarbondioxide), 3103
1,3-Pentadiyne, 1819
2-Penten-4-yn-3-ol, 1873
Phenoxyacetylene, 2915
Phenyl, phenylethynyliodonium perchlorate, 3628
Poly(2,4-hexadiyne-1,6-ylene carbonate), 2665
Potassium acetylene-1,2-dioxide, 0986
Potassium ethynediolate, 0986
Potassium hydrogen acetylenedicarboxylate, 1378
5-(Prop-2-ynyloxy)-1,2,3,4-thiatriazole, 1416
Propiolaldehyde, 1082
Propiolic acid, 1083
Propioloyl chloride, 1062
3-Propynethiol, 1148
3-Propynol, 1144
2-Propynyl vinyl sulfide, 1877
Sodium ethynediolate, 1019
1,2:5,6:11,12:15,16-Tetrabenzocycloconta-1,5,11,15-tetraene-3,7,9,13,17,19-hexayne, 3882
Tetracyclo[20.2.0.$0^{6,9}$.$0^{14,17}$]tetracosa-1(22),6(9),14(17)-triene-2,4,10,12,18,20-hexayne-7,8,15,16,23,24-hexone, 3852
1,3,5-Triethynylbenzene, 3437
* Triethynylphosphine, 2117

ACETYLENIC PEROXIDES
ALKYNES
COMPLEX ACETYLIDES
ETHOXYETHYNYL ALCOHOLS
HALOACETYLENE DERIVATIVES
METAL ACETYLIDES
See ROTANES
See also PEROXIDISABLE COMPOUNDS

Metals

Chemical Intermediates, 1972 Catalogue, 158, Tamaqua (Pa.), Air Products and Chemicals Inc., 1972

Acetylenic compounds with replaceable acetylenically bound hydrogen atoms must be kept out of contact with copper, silver, magnesium, mercury or alloys containing them, to avoid formation of explosive metal acetylides.

See METAL ACETYLIDES

ACETYLENIC PEROXIDES $C{\equiv}C—C—OOH$

1. Milas, N. A. *et al., Chem. Eng. News*, 1959, **37**(37), 66
2. Milas, N. A. *et al., J. Amer. Chem. Soc.*, 1952, **75**, 1472; 1953, **76**, 5970

The importance of strict temperature control [1] to prevent explosion during the preparation [2] of acetylenic peroxides is stressed. Use of inert solvent to prevent undue increase in viscosity which leads to poor temperature control is recommended [1].

Individually indexed compounds are:

2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3703
2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3705

See other PEROXIDES

ACID ANHYDRIDES RCO.OCO.R, RSO_2OSO_2R

The several members of this reactive group involved in hazardous incidents are:

Acetic anhydride, 1529
Benzeneseleninic anhydride, 3489
Benzenesulfonic anhydride, 3492
* Chromium trioxide, 4236
Dichloromaleic anhydride, 1355
* Dinitrogen pentaoxide, 4743
Disulfur heptaoxide, 4864
* Disulfuryl dichloride, 4097
* Disulfuryl difluoride, 4320
Maleic anhydride, 1400
* Methaneboronic anhydride—pyridine complex, 0426
* Peroxypropionyl nitrate, 1183
* Peroxypropionyl perchlorate, 1163
Phthalic anhydride, 2894
* Pivaloyloxydiethylborane, 3192
† Propadiene-1,3-dione, 1345
Succinic anhydride, 1439
Sulfur trioxide, 4843
* Sulfur trioxide—dimethylformamide, 4844
Tetraphosphorus decaoxide, 4866
Trifluoroacetic anhydride, 1362
Trifluoroacetyl trifluoromethanesulfonate, 1054

ACRYLIC MONOMERS $CH_2=C(X)C=O$

Schulze, S. *et al., Chem. Eng. Technol*, 1998, **21**, 829

Most of these monomers are inclined to violent polymerisation unless stabilised. Stabilisation usually involves oxygen as well as the nominal stabiliser. A kinetic study of the process for acrylic and methacrylic acids is reported.

See VIOLENT POLYMERISATION

See also POLYMERISATION INCIDENTS

ACYL AZIDES $RCO.N_3$, $-SO_2N_3$, $-P(O)N_3$

1. Smith, P. A. S., *Org. React.*, 1946, **3**, 373—375
2. Houben-Weyl, 1952, Vol. 8, 680
3. Lieber, E. *et al., Chem. Rev.*, 1965, **65**, 377
4. Balabanov, G. P. *et al., Chem. Abs.*, 1969, **70**, 59427
5. Renfrow, W. B. *et al., J. Org. Chem.*, 1975, **40**, 1526
6. Anon., *Sichere Chemiarb.*, 1984, **36**, 143—144
7. Hazen, G. G. *et al., Synth. Comm.*, 1981, **11**(12), 947
8. Tuma, L. D. *Thermochim. Acta.*, 1994, **243**(2), 161
9. Tuma, L. D. *et al., Synlett*, 1996, (5), 407
10. Green, G. M., *et al., J. Org. Chem.*, 2001, **66**(7), 2509

Azides of low molecular weight (more than 25% nitrogen content) should not be isolated from solution, as the concentrated material is likely to be dangerously explosive [1]. The concentration of such solutions (prepared below 10°C) should be $< 10\%$ [2]. Carbonyl azides are explosive compounds, some exceptionally so, and suitable handling precautions are necessary [3]. The sensitivity to friction, heat and impact of benzenesulfonyl azide, its 4- chloro-, methyl-, methoxy-, methoxycarbonylamino-, and nitro- derivatives, and 1,3-benzenedisulfonyl diazide were studied [4]. Benzenesulfonyl azide and 2-toluenesulfonyl azide may be smoothly thermolysed in benzene [5]. In this Curtius procedure for rearrangement with loss of nitrogen to isocyanates, it is important to ensure (by IR examination) that the products of such rearrangements are substantially free of residual acyl azide before attempting distillation of the material. Failure to make this check led to a violent explosion of 70 g of an unspecified crude isocyanate when the distillation flask was immersed in a preheated oil-bath [6]. Further mishaps have provoked further studies: Tests for safety as reagents for azo transfer were conducted on five arylsulfonyl azides. It was concluded that toluenesulfonyl azide (with the lowest molecular weight) was the least safe, of shock sensitivity and power variously compared with TNT and tetryl (and elsewhere with nitroglycerine). [Such power seems thermodynamically implausible, it is assigned only 80 kcal/mole, 1.7 kJ/g.] The safest was 4-dodecylbenzenesulfonyl azide (with the highest m.w.). Thermally most stable was 4-carboxybenzenesulfonylazide, but its decomposition rate was highest once started, it was marginally shock sensitive [7]. Another safety study of sulfonyl azides, including detonation, also preferred dodecylbenzenesulfonyl azide [8]. Further work has been published, this found 2,4,6-triisopropylbenzene sulfonyl azide perhaps the most useful, and also showed naphthalene-2-sulfonyl azide to be relatively safe as a reagent [9]. A polymer supported benzenesulfonyl azide reagent is claimed as safe and efficient [10].

Individually indexed compounds are:

Acetyl azide, 0767
Azidocarbonyl fluoride, 0338
4-Azidocarbonyl-1,2,3-thiadiazole, 1066
N-Azidocarbonylazepine, 2724
* Azidocarbonylguanidine, 0816
Azidodithioformic acid, 0385
Benzene-1,3-bis(sulfonyl azide), 2203
Benzenesulfinyl azide, 2266
Benzenesulfonyl azide, 2267
Benzoyl azide, 2694
4,4’-Biphenylene-bis-sulfonylazide, 3461
cis-1,2-Bis(azidocarbonyl)cyclobutane, 2316
1,2-Bis(azidocarbonyl)cyclopropane, 1829
Bis(azidothiocarbonyl) disulfide, 1012
4-Bromobenzoyl azide, 2640
tert-Butyl azidoformate, 1930
N-Butylamidosulfuryl azide, 1687
Carbonic diazide, 0547
Carboxybenzenesulfonyl azide, 2695
4-Chlorobenzenesulfonyl azide, 2145
4-Chlorobenzoyl azide, 2650
N-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide, 1128
Cyanodiazoacetyl azide, 1342
Cyanohydrazonoacetyl azide, 1080
1,2-Diazidocarbonylhydrazine, 0716
Diazoacetyl azide, 0675
Disulfuryl diazide, 4774
Ethyl azidoformate, 1189
Fluorothiophosphoryl diazide, 4302
2-Furoyl azide, 1815
Glutaryl diazide, 1868
4-Methylaminobenzene-1,3-bis(sulfonyl azide), 2781
4-Nitrobenzenesulfinyl azide, 2197
Palladium(II) azidodithioformate, 1011
Phenylphosphonic azide chloride, 2226
Phenylphosphonic diazide, 2277
3-Phenylpropionyl azide, 3138
Phenylthiophosphonic diazide, 2278
Phthaloyl diazide, 2893
Pivaloyl azide, 1929
Potassium azidodisulfate, 4650
Potassium azidosulfate, 4648
6-Quinolinecarbonyl azide, 3237
* Silver azidodithioformate, 0302
Sodium azidosulfate, 4754

Succinoyl diazide, 1434
Sulfamoyl azide, 4466
Sulfinyl azide, 4772
Sulfuryl azide chloride, 4025
Sulfuryl diazide, 4773
* Thallium(I) azidodithiocarbonate, 0540
4-Toluenesulfinyl azide, 2776
4-Toluenesulfonyl azide, 2777
Trifluoroacetyl azide, 0623
N-(Trifluoromethylsulfinyl)trifluoromethylimidosulfinyl azide, 0636
Trifluoromethylsulfonyl azide, 0347
1,3,5-Tris(4-azidosulfonylphenyl)-1,3,5-triazinetrione, 3812

See also 2-AZIDOCARBONYL COMPOUNDS, CUBANES, SULFINYL AZIDES

ACYL CHLORIDES RCO.Cl

Aromatic hydrocarbons, Trifluoromethanesulfonic acid

See Trifluoromethanesulfonic acid: Acyl chlorides, etc.

ACYL HALIDES RCO.X, -SO.X, -SO$_2$X

This group tends to react violently with protic organic solvents, water, and the aprotic solvents, dimethylformamide and dimethyl sulfoxide. Their facile reaction with ethers is also potentially hazardous.

Individually indexed compounds are:

Acetyl bromide, 0724
† Acetyl chloride, 0731
† Acryloyl chloride, 1090
Azidocarbonyl fluoride, 0338
Benzenesulfinyl chloride, 2227
Benzenesulfonyl chloride, 2228
Benzoyl chloride, 2671
* Benzyl chloroformate, 2926
tert-Butyl chloroperoxyformate, 1920
† Butyryl chloride, 1550
* Carbonyl dichloride, 0328
* Carbonyl difluoride, 0342
* Chlorine fluorosulfate, 3969
(Chlorocarbonyl)imidosulfur difluoride, 0317
N-(Chlorocarbonyloxy)trimethylurea, 1918
* Chlorosulfonyl isocyanate, 0323
Chlorosulfuric acid, 3991
* Chromyl fluorosulfate, 4219
Cyanoacetyl chloride, 1072
Cyanoformyl chloride, 0597
4,4-Diferrocenylpentanoyl chloride, 3853
2,2-Dinitro-2-fluoroethoxycarbonyl chloride, 1069

Disulfuryl dichloride, 4097
Disulfuryl difluoride, 4320
† Ethyl chloroformate, 1160
Ethyl oxalyl chloride, 1452
N-Ethyl-*N*-propylcarbamoyl chloride, 2462
* Fluorine fluorosulfate, 4318
Furoyl chloride, 1812
2,4-Hexadiynylene chloroformate, 2885
2,4-Hexadiynylene chlorosulfite, 2155
† Isobutyryl chloride, 1553
Isophthaloyl chloride, 2883
† Isopropyl chloroformate, 1555
Methanesulfinyl chloride, 0434
Methoxyacetyl chloride, 1161
4-Methoxybenzoyl chloride, 2925
† Methyl chloroformate, 0732
Oleoyl chloride, 3766
Oxalyl dibromide, 0580
Oxalyl dichloride, 0602
* Oxopropanedinitrile, 1337
Pentafluoropropionyl fluoride, 1051
Peroxodisulfuryl difluoride, 4322
* Phenylphosphonyl dichloride, 2238
† Pivaloyl chloride, 1919
Propioloyl chloride, 1062
† Propionyl chloride, 1159
Sebacoyl chloride, 3335
Sulfinyl chloride, 4090
Sulfonyl chloride, 4093
Sulfur oxide-(*N*-fluorosulfonyl)imide, 4299
Sulfuryl azide chloride, 4025
Terephthaloyl chloride, 2884
* 2,4,6-Trichloro-1,3,5-triazine, 1035
Trifluoroacryloyl fluoride, 1046
Trifluoromethanesulfenyl chloride, 0321
Trifluoromethanesulfinyl fluoride, 0353

See Propionyl chloride: Diisopropyl ether

O-ACYLHYDROXAMIC ACIDS HOC(R)=NOCOR′

Houben Weyl 10/4, 1968, 232

Warning is given against dry distillation of the alkali salts as an isocyanate preparation. The decomposition is often explosive

See other N—O COMPOUNDS

ACYL HYPOHALITES RCO.OX

1. Tari, I. *et al., Inorg. Chem.*, 1979, **18**, 3205—3208
2. Skell, P. S. *et al., J. Amer. Chem. Soc.*, 1983, **105**, 4000, 4007

Sodium salts of fluoroacids react with chlorine fluoride at —112 to —78°C to give explosively unstable fluoroacyl hypochlorites. Trifluoroacetyl hypochlorite and its pentafluoropropionyl, heptafluorobutyryl, difluoroacetyl and chlorodifluoroacetyl analogues explode without fail if the partial pressure exceeds 27—67 mbar. Hexafluoroglutaryl dihypochlorite explodes above —10°C [1]. Of the 4 compounds prepared, acetyl, propionyl, isobutyryl and pivaloyl hypobromites, the 2 latter appeared stable indefinitely at —41°C in the dark, while the 2 former exploded unpredictably as isolated solids [2].

Individually indexed compounds are:

Acetyl hypobromite, 0725
Acetyl hypofluorite, 0748
Caesium fluoroxysulfate, 4250
Chlorodifluoroacetyl hypochlorite, 0600
Difluoroacetyl hypochlorite, 0649
Fluorine fluorosulfate, 4318
Heptafluorobutyryl hypochlorite, 1348
Heptafluorobutyryl hypofluorite, 1365
Hexafluoroglutaryl dihypochlorite, 1800
Pentafluoropropionyl hypochlorite, 1030
Pentafluoropropionyl hypofluorite, 1053
Propionyl hypobromite, 1150
Rubidium fluoroxysulfate, 4303
Trifluoroacetyl hypochlorite, 0591
Trifluoroacetyl hypofluorite, 0629

See Acetyl hypobromite, Propionyl hypobromite

ACYL NITRATES RCO.ONO$_2$

A thermally unstable group of compounds, tending to violent decomposition or explosion on heating. Individually indexed compounds are:

Acetyl nitrate, 0761
Benzoyl nitrate, 2685
Butyryl nitrate, 1568
3-Nitrobenzoyl nitrate, 2660
* Peroxyacetyl nitrate, 0762
* Peroxypropionyl nitrate, 1183

See Nitric acid: Phthalic anhydride, etc.

ACYL NITRITES RCO.ON:O

1. Ferrario, E., *Gazz. Chim. Ital. [2]*, 1901, **40**, 98—99
2. Francesconi, L. *et al., Gazz. Chim. Ital. [1]*, 1895, **34**, 442

The stabilities of propionyl nitrite and butyryl nitrite are greater than that of acetyl nitrite, butyryl nitrite being the least explosive of these homologues [1]. Benzyl nitrite is also unstable [2]. Individual compounds are:

Acetyl nitrite, 0759
Heptafluorobutyryl nitrite, 1364
Propionyl nitrite, 1181
Trifluoroacetyl nitrite, 0622

See Sodium nitrite: Phthalic acid, etc.

ADHESIVE LABELS

Tolson, P. *et al., J. Electrost.*, 1993, **30**, 149

A heavy duty lead-acid battery exploded when an operator peeled an adhesive label from it. Investigation showed that this could generate >8 kV potential. Discharge through the hydrogen/oxygen headspace consequent upon recharging batteries caused the explosion. The editor has remarked very vivid discharges when opening Chemical Society self-adhesive envelopes.

See STATIC INITIATION INCIDENTS

ADIABATIC CALORIMETRY

1. Hub, L., *Runaway Reactions*, 1981, Paper 3/K, 1—11
2. Hakl, J., *Runaway Reactions*, 1981, Paper 3/L, 1—11
3. Brogli, F. *et al., Runaway Reactions*, 1981, Paper 3/M, 1—10
4. Townsend, D. I., *Runaway Reactions*, 1981, Paper 3/Q, 1—14
5. Cardillo, P. *et al., J. Haz. Mat.*, 1984, **9**, 224

The Sikarex safety calorimeter system and its application to determine the course of adiabatic self-heating processes, starting temperatures for self-heating reactions, time to explosion, kinetic data, and simulation of real processes, are discussed with examples [1]. The Sedex (sensitive detection of exothermic processes) calorimeter uses a special oven to heat a variety of containers with sophisticated control and detection equipment, which permits several samples to be examined simultaneously [2]. The bench-scale heat-flow calorimeter is designed to provide data specifically oriented towards processing safety requirements, and a new computerised design has become available [3]. The accelerating rate calorimeter is the most sophisticated and sensitive of the techniques, and it is claimed that very close parallels with large-scale process operations can be simulated [4].

See ACCELERATING RATE CALORIMETRY, ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY, HEAT FLOW CALORIMETRY

AGITATION INCIDENTS

Weir, D. E., *Plant/Oper. Progr.*, 1986, **5**, 142—147

The relationship of agitation problems (failure, incomplete mixing, shear energy input) with thermal runaway reactions and ways of avoiding these, are discussed.

Several of the runaway reactions or violent incidents in the main text were caused by ineffective agitation or by the complete absence of agitation, particularly in reactions between 2 phases of widely differing densities. Individual cases involved are:

2-Chloronitrobenzene, 2134
Chromyl chloride, 4048

Diethyl 4-nitrophenyl thionophosphate, 3322
Ethylmagnesium iodide, 0855
Hydrogen peroxide, : Iron(II) sulfate, 2-Methylpyridine, Sulfuric acid, 4471
Lead(IV) oxide, : Carbon black, Chlorinated paraffin, Manganese(IV) oxide, 4828
Lithium tetrahydroaluminate, : Fluoroamides, 0075
4-Methyl-2-nitrophenol, 2763
Nitric acid, : 1-Nitronaphthalene, Sulfuric acid, 4430
Nitric acid, : 2-Formylamino-1-phenyl-1,3-propanediol, 4430
Nitric acid, : *tert*-Butyl-*m*-xylene, Sulfuric acid, 4430
Nitric acid, : Hydrocarbons, 4430
Nitric acid, : Nitrobenzene, Sulfuric acid, 4430
2-Nitrotoluene, : Alkali, 2759
Phosphorus tribromide, : Phenylpropanol, 0292
Potassium hydroxide, : Water, 4422
Sodium carbonate, 0549
Sodium dichromate, : Sulfuric acid, Trinitrotoluene, 4244
Sodium hydrogen carbonate, : Carbon, Water, 0389
Sulfinyl chloride, : Tetrahydrofuran, 4090
Sulfuric acid, : 2-Aminoethanol, 4473
Sulfuric acid, : 4-Methylpyridine, 4473
Tetrachlorosilane, : Ethanol, Water, 4167
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

AIR

1. Anon., *Site Safe News*, 1991, Summer, (HSE, Bootle, UK)
2. Allan, M., *CHAS Notes*, 1991, **IX**(5), 2
3. Sagan, C. *et al., Nature*, 1993, **365**(6448), 720

A dangerous oxidant by virtue of its oxygen content, responsible for almost all fires, dust and vapour-cloud explosions, and for many other incidents. When heated to decomposition, air produces fumes of highly toxic nitrogen oxides. Air is frequently encountered compressed in combustible containers (tyres) which can explode with fatal results. Sometimes combustion seems to be the cause of the burst, this may be attributed to excessive heating and prior decomposition reactions generating a gaseous fuel [1]. Another fuel source causing a similar burst was an emergency inflator powered by liquid propane/butane [2]. Under cryogenic conditons, air may spontaneously fractionate, concentrating the hazard in residues which are effectively liquid oxygen. The editor has been told that air can be explosive in its own right in a eucalyptus wood on a hot day, and, having smelt one, does not find this absolutely incredible. Explosive air is sometimes also found in caves and mines when decaying vegetable matter is present. From a theoretical and thermodynamic standpoint, air should be considered a poison to carbon-based life [3]. Handle with due caution.
See also BATS, DIESEL ENGINES

ALDEHYDES **RCO.H**

1. Editor's comments, 1995
2. Britton, L. B. *Process Saf. Progr.*, 1998, **17**(2), 138

These materials are very easily autoxidised and often have a low autoignition temperature. It is reported that many of the less volatile liquid aldehydes will eventually inflame if left exposed to air on an absorbent surface. The mechanism is undoubtedly similar to that giving rise to easy ignition in the air-oxidation of acetaldehyde and propionaldehyde; initial formation of a peroxy-acid which catalyses the further oxidation [1]. Autoignition temperatures of lower aldehydes are much reduced by pressure, but appear to depend little on oxygen content. The effect is worst in the presence of free liquid, in which initial oxidation appears to occur, possibly catalysed by iron, followed by ignition of the vapour phase. An acetaldehyde/rust mix exploded at room temperature on increasing the air pressure to 7 bar. It is suggested that the measurement criteria for ignition in the ASTMS standard lower oxygen concentration test are unsuitable [2]. The acid catalysed oligomerisation whereby the C=O bond converts to a, usually cyclic trimeric, polyacetal structure is sufficiently exothermic to be potentially dangerous for the smaller members of the series: it has ruptured large acetaldehyde containers on occasion and would be extremely hazardous were monomeric formaldehyde handled as a liquid.

Individually indexed compounds are:

† Acetaldehyde, 0824
4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3260
4-Acetoxy-3-methoxybenzaldehyde, 3284
† Acrylaldehyde, 1142
4-Azidobenzaldehyde, 2693
† Benzaldehyde, 2727
† Butyraldehyde, 1602
5-Chloro-2-nitrobenzaldehyde, 2648
4-Chloro-3-nitrobenzaldehyde, 2647
2-Chloro-6-nitrobenzaldehyde, 2646
∗ Chloroacetaldehyde oxime, 0783
Cinnamaldehyde, 3128
† Crotonaldehyde, 1513
† 2-Ethylhexanal, 3045
† Formaldehyde, 0415
2-Furaldehyde, 1830
4-Hydroxy-3-methoxybenzaldehyde, 2953
4-Hydroxy-3-nitrobenzaldehyde, 2687
3-Hydroxy-4-nitrobenzaldehyde, 2686
2-Indanecarboxaldehyde, 3282
† Isobutyraldehyde, 1606
† Isovaleraldehyde, 1952
† Methacrylaldehyde, 1519
3-Methoxy-2-nitrobenzaldehyde, 2932
4-Methoxybenzaldehyde, 2951
2-Nitroacetaldehyde, 2682
∗ 2-Nitroacetaldehyde oxime, 0805
3-Nitrobenzaldehyde, 2683
4-Nitrobenzaldehyde, 2684

Paraformaldehyde, 0416
α-Pentylcinnamaldehyde, 3656
Propionaldehyde, 1220
Tridecanal, 3613
† Valeraldehyde, 1960

See Acetaldehyde

See also INSULATION, PAPER TOWELS, PEROXIDISABLE COMPOUNDS

ALKALI-METAL ALLOYS

1. Mumford, C., *Chem. Brit.*, 1978, **14**, 170
2. Ingham, P. L., *Chem. Brit.*, 1978, **14**, 326
3. Bretherick, L., *Chem. Brit.*, 1978, **14**, 426
4. Sloan, S. A., *Chem. Brit.*, 1978, **14**, 597

In response to a statement [1] that alloys of 2 alkali-metals (Li—Na, K—Na) can be prepared in small amounts by beating the solid components together, without heating in the latter case, it was emphasised that the real hazard arises not from reaction of the surface coating of potassium superoxide with potassium, but with residues of oil or organic matter on the potassium which will explode under impaction with the superoxide [2]—[4].

See Potassium (*slow oxidation*)

See also ALKALI METALS BELOW

ALKALI-METAL DERIVATIVES OF HYDROCARBONS RM, ArM

1. Sidgwick, 1950, 68, 75
2. Leleu, *Cahiers*, 1977(88), 370

Alkali-metal derivatives of aliphatic or aromatic hydrocarbons, such as methyllithium, ethylsodium or phenylpotassium, are the most reactive towards moisture and air, immediately igniting in the latter. Derivatives of benzyl compounds, such as benzylsodium, are of slightly lower activity, usually but not always igniting in air. Derivatives of hydrocarbons with definitely acidic hydrogen atoms (acetylene, phenylacetylene, cyclopentadiene, fluorene), though readily oxidised, are usually relatively stable in ambient air. Sodium phenylacetylide if moist with ether, ignites; derivatives of triphenylmethane also when dry [1]. Biphenyl-, naphthyl-, anthryl- and phenanthrylsodium may all ignite in air when finely divided, and all react violently with water [2].

Specific compounds may be found in the groups:

ALKYLMETALS
ARYLMETALS
ORGANOMETALLICS

ALKALI METALS

1. *Handling and Uses of the Alkali Metals* (Advances in Chemistry Series No. 19), Washington, ACS, 1957
2. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633—636
3. *Alkali Metal Dispersions*, Fatt, I. *et al.*, London, Van Nostrand, 1961
4. John, G. D., *School Sci. Rev.*, 1980, **62**(219), 279—286
5. Roesky, H. W., *Inorg. Chem.*, 2001, **40**(26), 6855

The collected papers of a symposium at Dallas, April 1956, cover all aspects of the handling, use and hazards of lithium, sodium, potassium, their alloys, oxides and hydrides, in 19 chapters [1]. Interaction of all 5 alkali metals with water under various circumstances has been discussed comparatively [2]. In a monograph covering properties, preparation, handling and applications of the enhanced reactivity of metals dispersed finely in hydrocarbon diluents, the hazardous nature of potassium dispersions, and especially of rubidium and caesium dispersions is stressed [3]. Alkaline-earth metal dispersions are of relatively low hazard. Safety practices for small-scale storage, handling, heating and reactions of lithium potassium and sodium with water are reviewed [4]. A safe method for the disposal of trivial quantities of potassium and sodium by controlled hydrolysis has been published [5].

See Potassium (reference 6)

ALKANETHIOLS RSH

Nitric acid

Individually indexed compounds are:

Ethylene oxide

See Ethylene oxide: Alkanethiols

† 2-Butanethiol, 1707
† Butanethiol, 1706
Dodecanethiol, 3561
† Ethanethiol, 0929
† Methanethiol, 0487
† 2-Methyl-2-propanethiol, 1710
† 2-Methylbutane-2-thiol, 2017
† 3-Methylbutanethiol, 2018
† 2-Methylpropanethiol, 1709
† Pentanethiol, 2019
† 2-Propanethiol, 1286
† Propanethiol, 1285

See Nitric acid: Alkanethiols

ALKENEBIS(SULFONIUM PERCHLORATES)

Shine, H. J. *et al., J. Org. Chem.*, 1979, **44**, 915—917

The perchlorate salts of the bis-adducts of thianthrene (X = S) or phenoxathiin (X = O) with substituted acetylenes explode on heating.

See THIANTHRENIUM PERCHLORATE

See other NON-METAL PERCHLORATES

ALKENES —C=C—

Oxides of nitrogen

Simmons, H. E. *et al., Chem. Eng. News*, 1995, **73**(32), 4

Several nitrogen oxides; dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide; can readily add to alkenes; the resultant nitronitroso- dinitro- and nitronitrato-alkanes will be explosive if of low molecular weight and impurities make them more so. The tendency of nitroso compounds to exist as insoluble dimers, which precipitate and thus concentrate, makes dinitrogen trioxide a more hazardous contaminant than its higher homologues.

† 1-Butene, 1572
† *cis*-2-Butene, 1573
† *trans*-2-Butene, 1574
∗ Δ3-Carene, 3330
† Cyclobutene, 1479
cis-Cyclododecene, 3345
† Cycloheptene, 2833
† Cyclohexene, 2400
† Cyclopentene, 1885
∗ 2-Deuterobicyclo[2.2.1]hept-2-ene, 2807
† 2,6-Dimethyl-3-heptene, 3184
∗ 1,1-Diphenylethylene, 3635
∗ *trans*-1,2-Diphenylethylene, 3636
† Ethylene, 0777
† 3-Heptene, 2849
† 1-Heptene, 2847
† 2-Heptene, 2848
† 2-Hexene, 2454
† 1-Hexene, 2453
† 2-Methyl-1-pentene, 2456
† 4-Methyl-1-pentene, 2457
† *cis*-4-Methyl-2-pentene, 2458
† *trans*-4-Methyl-2-pentene, 2459
† 4-Methylcyclohexene, 2835
† 2-Methylpropene, 1577
† 1-Octene, 3035
† 2-Octene, 3036
∗ 2-Pinene, 3333
† Propene, 1194
∗ 1-Pyrrolidinylcyclohexene, 3344
∗ Styrene, 2940
† 2,3,4-Trimethyl-1-pentene, 3037
† 2,4,4-Trimethyl-1-pentene, 3038
† 2,3,4-Trimethyl-2-pentene, 3039
† 2,4,4-Trimethyl-2-pentene, 3040
† 3,4,4-Trimethyl-2-pentene, 3041
† 2,3,3-Trimethylbutene, 2851
† Vinylcyclohexane, 3021

Individually listed alkenes are:
See 2-Chloro-1,3-butadiene: Preparative hazard
See Nitrogen oxide: Dienes, Oxygen

ALKENYL NITRATES —C=C—ONO$_2$

Tetrafluorohydrazine

See Tetrafluorohydrazine: Alkenyl nitrates

See related ALKYL NITRATES

ALKYLALUMINIUM ALKOXIDES AND HYDRIDES R$_2$AlOR', R$_2$AlH

Although substitution of a hydrogen atom or an alkoxy group for one alkyl group in a trialkylaluminium tends to increase stability and reduce reactivity and the tendency to ignition, these compounds are still of high potential hazard, the hydrides being used industrially as powerful reducants.

Individually indexed compounds of this relatively small sub-group of commercially available compounds are:

Diethylaluminium hydride, 1713
Diethylethoxyaluminium, 2549
Diisobutylaluminium hydride, 3076
Dimethylaluminium hydride, 0932
Dipropylaluminium hydride, 2547
* 4-Ethoxybutyldiethylaluminium, 3366
Ethoxydiisobutylaluminium, 3367
Tetramethyldialuminium dihydride, 1772
* Triethoxydialuminium tribromide, 2550

See ALKYLALUMINIUM DERIVATIVES (references 1,3,6)

Ethers

Wissink, H. G., *Chem. Eng. News*, 1997, **75**(9), 6

Dialkylaluminium hydrides can cleave lower ethers to generate gaseous products (hydrocarbons and/or hydrogen), which may pressurise and burst containers if solutions in ethers be stored.

ALKYLALUMINIUM DERIVATIVES

1. Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **53**(1), 53A—56A
2. Heck, W. B. *et al., Ind. Eng. Chem.*, 1962, **54**(12), 35—38
3. Kirk-Othmer, 1963, Vol. 2, 38, 40
4. Houben-Weyl, 1970, Vol. 13.4, 19
5. ‘Aluminium Alkyls’, Brochure PB 3500/1 New 568, New York, Ethyl Corp., 1968
6. ‘Aluminium Alkyls’, New York, Texas Alkyls, 1971
7. Knap, J. E. *et al., Ind. Eng. Chem.*, 1957, **49**, 875
8. Thomas, W. H., *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**(1), 120—122
9. Van Vliet, M. R. P. *et al., Organometallics*, 1987, **6**, 1652—1654

This main class of ALKYLALUMINIUM DERIVATIVES is divided for structural convenience into the 3 groups: TRIALKYLALUMINIUMS; ALKYLALUMINIUM ALKOXIDES AND HYDRIDES; and ALKYLALUMINIUM HALIDES.

Individual compounds are indexed under their appropriate group titles, but since most of the available compounds are liquids with similar hazardous properties, these will be described collectively here. These aspects of the class have been extensively reviewed and documented [1,2,3,4,5,6,7,8].

Compounds with alkyl groups of C_4 and below all ignite immediately on exposure to air, unless diluted with a hydrocarbon solvent to 10—20% concentration [6]. Even these solutions may ignite on prolonged exposure to air, owing to exothermic autoxidation, which becomes rapid if solutions are spilled (high surface:volume ratio) [2,6]. Compounds with C_5—C_{14} alkyl groups (safe at 20—30% conc.) smoke in air but do not burn unless ignited externally or if the air is very moist. Contact with air enriched with oxygen above the normal 21% content will cause explosive oxidation to occur.

Fires involving alkylaluminium compounds are difficult to control and must be treated appropriately to particular circumstances [1,5,6], usually with dry-powder extinguishers. Halocarbon fire extinguishants (carbon tetrachloride, chlorobromomethane, etc.), water or water-based foam must not be applied to alkylaluminium fires. Carbon dioxide is ineffective unless dilute solutions are involved [5,6]. Suitable handling and disposal procedures have been detailed for both laboratory [1,2,5,6,7] and manufacturing [5,6] scales of operation.

See ALKYLALUMINIUM ALKOXIDES AND HYDRIDES, ALKYLALUMINIUM HALIDES, TRIALKYLALUMINIUMS

Alcohols

Alkylaluminium derivatives up to C_4 react explosively with methanol or ethanol, and triethylaluminium also with 2-propanol.

Halocarbons

With the exception of chlorobenzene and 1,2-dichloroethane, halocarbon solvents are unsuitable diluents, as carbon tetrachloride and chloroform may react violently with alkylaluminium derivatives. The hazards of individually mixing 7 alkylaluminiums with 7 chlorinated solvents have been assessed comparatively. Most of a series of cyclic coordination complexes between triethylaluminium and α-iminoketones decomposed violently when dissolved in halogenated solvents.

Oxidants

In view of the generally powerfully reducing properties of alkylaluminium derivatives, deliberate contact with known oxidants must be under careful control with appropriate precautions.

Water

Interaction of alkylaluminium derivatives up to C_9 chain length with liquid water is explosive and violent shock effects have been noted [4].

See other ALKYLMETAL HALIDES, ALKYLMETAL HYDRIDES, ALKYLMETALS

ALKYLALUMINIUM HALIDES $RAlX_2$, R_2AlX, $R_3Al.AlX_3$

Three main structural sub-groups can be recognised: alkylaluminium dihalides, dialkylaluminium halides, and trialkyldialuminium trihalides (equimolar complexes of a trialkylaluminium and an aluminium trihalide). While this is generally a very reactive group of compounds, similar in reactivity to trialkylaluminium compounds, increase in size of the alkyl groups present and in the degree of halogen substitution tends to reduce pyrophoricity.

Individually indexed compounds of this group many of which are commercially available in bulk are:

Diethylaluminium bromide, 1664
Diethylaluminium chloride, 1665
Diisobutylaluminium chloride, 3059
Dimethylaluminium bromide, 0878
Dimethylaluminium chloride, 0879
Ethylaluminium bromide iodide, 0837
Ethylaluminium dibromide, 0838
Ethylaluminium dichloride, 0839
Ethylaluminium diiodide, 0840
∗ Hexaethyltrialuminium trithiocyanate, 3688
Methylaluminium diiodide, 0422
Triethyldialuminium trichloride, 2551
Trimethyldialuminium trichloride, 1288

See ALKYLALUMINIUM DERIVATIVES (references 1,2)
See other ALKYLMETAL HALIDES

ALKYLBORANES RBH_2, R_2BH, R_3B

1. Sidgwick, 1950, 371
2. Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **53**(1), 53A
3. Brown, H. C. *et al., Tetrahedron*, 1986, **42**, 5523—5530

Trimethylborane and triethylborane ignite in air, and tributylborane ignites in a thinly diffused layer, as when poured on cloth [1]. Generally, the pyrophoric tendency of trialkylboranes decreases with increasing branching on the 2- and 3-carbon atoms of the alkyl substituent(s) [2]. Reaction of a trialkylborane with oxygen under controlled, mild and safe conditions gives high yields of the corresponding alkanols [3].

Individually indexed compounds are:

Bis(dibutylborino)acetylene, 3769
∗ *N,N*-Bis(diethylboryl)methylamine, 3217
Bis(dipropylborino)acetylene, 3663
Dibutyl-3-methyl-3-buten-1-ynlborane, 3612
† 1,2-Dimethylborane, 0957
† 1,1-Dimethyldiborane, 0956
Ethylpentaborane(9), 0969
∗ Methylborylene, 0424
Methyldiborane, 0510
∗ Perhydro-9*b*-boraphenalene, 3544
∗ 1-Phenylboralane, 3311
∗ Pivaloyloxydiethylborane, 3192
‘Tetraethyldiborane’, 3092
Tetramethyldiborane, 1773
‘Tetrapropyldiborane’, 3574
Tri-2-butylborane, 3564
mixo-Tributylborane, 3563

Triethylborane, 2554
Triethyldiborane, 2584
Trimethylborane, 1291
Trimethyldiborane, 1330
Tripropylborane, 3211
* Tris(dimethylfluorosilylmethyl)borane, 3218

See other ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

ALKYL CHLORITES ROCl:O

Chlorite esters, like chlorite salts, are explosively unstable.

See Silver chlorite, Alone, or Iodoalkanes

See also CHLORITE SALTS

ALKYLHALOBORANES RBX_2, R_2BX

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

* Bis(difluoroboryl)methane, 0393
Bromodimethylborane, 0883
Butyldichloroborane, 1624
Chlorodibutylborane, 3060
Chlorodiethylborane, 1667
Chlorodipropylborane, 2529
Dibromomethylborane, 0425
Dichloroethylborane, 0841
* Dichlorophenylborane, 2215

See other ALKYLNON-METAL HALIDES

ALKYLHALOPHOSPHINES RPX_2, R_2PX

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

* 1,2-Bis(dichlorophosphino)ethane, 0793
Bis(trifluoromethyl)chlorophosphine, 0594
* Bis(trifluoromethyl)cyanophosphine, 1050
tert-Butyldifluorophosphine, 1641
Chlorodimethylphosphine, 0895
Di-*tert*-butylfluorophosphine, 3062
Dichloromethylphosphine, 0437
Difluorotrifluoromethylphosphine, 0360
Difluorotrifluoromethylphosphine oxide, 0359
Fluorobis(trifluoromethyl)phosphine, 0642
* Fluorobis(trifluoromethyl)phosphine oxide, 0641
* Tetrachlorotrifluoromethylphosphorane, 0332

See other ALKYLNON-METAL HALIDES

ALKYLHALOSILANES **$RSiX_3$, $RSiHX_2$, R_2SiX_2, R_2SiHX, R_3SiX**

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

Chloromethylphenylsilane, 2806
† Chlorotrimethylsilane, 1300
† Cyanotrimethylsilane, 1659
† Dichlorodiethylsilane, 1677
† Dichlorodimethylsilane, 0898
† Dichloroethylsilane, 0899
† Dichloromethylsilane, 0469
† Dichloromethylvinylsilane, 1204
† Iodotrimethylsilane, 1302
† Methyltrichlorosilane, 0438
† Trichloroethylsilane, 0850
† Trichlorovinylsilane, 0743
* Tris(dimethylfluorosilylmethyl)borane, 3218
See other ALKYLNON-METAL HALIDES

ALKYL HYDROPEROXIDES **ROOH**

Swern, 1970, Vol. 1, 19; 1971, Vol. 2, 1, 29
Most alkylhydroperoxides are liquid, the explosivity of the lower members (possibly owing to presence of traces of the dialkyl peroxides) decreasing with increasing chain length.

Individually indexed compounds are:

* 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide, 3541
Allyl hydroperoxide, 1222
* Barium methyl hydroperoxide, 0885
* Bis(2-hydroperoxy-2-butyl) peroxide, 3073
* Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide, 3560
* 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3150
* α-(4-Bromophenylazo)benzyl hydroperoxide, 3600
* α-(4-Bromophenylazo)phenylethyl α-hydroperoxide, 3641
tert-Butyl hydroperoxide, 1692
2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide, 3312
2-Cyclohexenyl hydroperoxide, 2429
1,1-Dichloroethyl hydroperoxide, 0790
3,5-Dimethyl-3-hexyl hydroperoxide, 3070
Ethyl hydroperoxide, 0921
1-Hydroperoxphenylethane, 2980
Isopropyl hydroperoxide, 1279
Methyl hydroperoxide, 0484
1,2- or 1,4-Bis(2-hydroperoxy-2-propyl)benzene, 3535
2-Phenyl-1,1-dimethylethyl hydroperoxide, 3326
2-Phenyl-2-propyl hydroperoxide, 3160
* α-Phenylazo-4-bromobenzyl hydroperoxide, 3601

- * α-Phenylazo-4-fluorobenzyl hydroperoxide, 3602
- * α-Phenylazobenzyl hydroperoxide, 3603
- * 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, 3306
- 2-Tetrahydrofuryl hydroperoxide, 1619

Transition metal complexes

Skibida, I. P., *Russ. Chem. Rev.*, 1975, 789—800

The kinetics and mechanism of decomposition of organic hydroperoxides in presence of transition metal complexes have been reviewed.

See also ALLYLIC HYDROPEROXIDES, α-PHENYLAZO HYDROPEROXIDES

ALKYLIMINIOFORMATE CHLORIDES (‘IMINOESTER HYDROCHLORIDES’) $RC(:N^+H_2)OR'\ Cl^-$

Preparative hazard

See Hydrogen chloride: Alcohols, etc.

ALKYLMETAL HALIDES RMX, RMX_2, R_2MX

This highly reactive group of organometallic compounds includes the groups and the individually indexed compounds:

- * Bis(chloromethyl)thallium chloride, 0792
- * Chloroethylbismuthine, 0888
- * Dichlorodi-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium, 3800
- Diethylbismuth chloride, 1670
- Diethylgold bromide, 1666
- Dimethylantimony chloride, 0896
- Dimethylbismuth chloride, 0889
- Ethylmagnesium iodide, 0855
- Methylmagnesium iodide, 0445
- Methylzinc iodide, 0446

ALKYLALUMINIUM HALIDES
GRIGNARD REAGENTS
TRIALKYLANTIMONY HALIDES

ALKYLMETAL HYDRIDES R_mMH_n

This small group shows high reactivity or instability, individual compounds being :

- * Chloroethylbismuthine, 0888
- Diethylgallium hydride, 1715
- Methylstibine, 0496

ALKYLMETALS

This reactive and usually pyrophoric class includes the groups and the individually indexed compounds:

- * Acetylenebis(triethyllead), 3665
- * Acetylenebis(triethyltin), 3666
- Allyllithium, 1173
- * Benzylsodium, 2783
- * Bis(1-chloroethylthallium chloride) oxide, 1586

* Bis(dimethylamino)dimethylstannane, 2593
* Bis(dimethylstibinyl) oxide, 1755
* Bis(dimethylthallium)acetylide, 2514
* Bis(trifluoromethyl)cadmium-1,2-dimethoxyethane adduct, 0584
* Bis(trimethylsilylmethyl)magnesium, 3093
3-Buten-1-ynyltriethyllead, 3351
* 1-Butoxyethyl 3-trimethylplumbylpropiolate, 3546
Butyllithium, 1646
tert-Butyllithium, 1647
Butylsodium, 1661
* 2-Chlorovinyltrimethyllead, 1983
Cyclopentadienylgold(I), 1833
Cyclopentadienylsodium, 1849
μ-Cyclopentadienyltrimethyltitanium, 3033
* Di-2-butenylcadmium, 3022
* 1,2-Diaminoethanebis(trimethylgold), 3099
Dibutylmagnesium, 3063
* Dibutylthallium isocyanate, 3187
Dibutylzinc, 3074
Diethyl telluride, 1711
Diethylberyllium, 1669
Diethylcadmium, 1671
* Diethyllead dinitrate, 1686
Diethylmagnesium, 1681
Diethylzinc, 1712
Diisobutylzinc, 3075
Diisopentylmercury, 3362
Diisopentylzinc, 3365
Diisopropylberyllium, 2530
Dimethyl-1-propynylthallium, 1932
Dimethylberyllium, 0886
* Dimethylberyllium-1,2-dimethoxyethane, 0887
Dimethylcadmium, 0890
Dimethylmagnesium, 0904
Dimethylmanganese, 0905
Dimethylmercury, 0903
Dimethyl(phenylethynyl)thallium, 3292
* (Dimethylsilylmethyl)trimethyllead, 2601
* Dimethyltin dinitrate, 0910
Dimethylzinc, 0931
Dipropylmercury, 2532
* Divinylmagnesium, 1494
* Divinylzinc, 1542
* Di-μ-methylenebis(methylpentamethylcyclopentadienyl)dirhodium, 3849
* Dodecamethyltetraplatinum(IV) perchlorate, 3581

* 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,5-dihydro-3*H*-pyrazole, 3605
* Ethylenedicaesium, 0794
Ethyllithium, 0858
Ethylsodium, 0873
μ,1,1'-Ferrocenediyldilithium, 3250
* Hexacyclohexyldilead, 3888
Hexamethyldiplatinum, 2602
* Hexamethylerbium—hexamethylethylenediaminelithium complex, 2588
Hexamethylrhenium, 2603
Hexamethyltungsten, 2605
* Lithium hexamethylchromate(3-), 2586
* Lithium pentamethyltitanate-bis(2,2'-bipyridine), 2036
* Lithium tetramethylchromate(II), 1738
3-Methyl-3-buten-1-ynyltriethyllead, 3407
* Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium), 3860
* Methylbismuth oxide, 0427
Methylcopper, 0439
Methylenedilithium, 0400
Methylenemagnesium, 0401
Methyllithium, 0451
Methylpotassium, 0447
Methylsilver, 0420
Methylsodium, 0462
Octylsodium, 3048
Pentamethyltantalum, 2040
Potassium cyclopentadienide, 1840
Propylcopper(I), 1247
Propyllithium, 1249
Propylsodium, 1265
* Tellurane-1,1-dioxide, 1974
* Tetraallyluranium, 3542
Tetraethyllead, 3089
Tetraethyltin, 3091
Tetraisopropylchromium, 3571
* Tetramethylbis(trimethysilanoxy)digold, 3376
Tetramethyldigallane, 1742
Tetramethyldistibane, 1763
Tetramethyllead, 1761
Tetramethylplatinum, 1762
Tetramethyltellurium(IV), 1766
† Tetramethyltin, 1765
* Tetravinyllead, 3011
* Triallylchromium, 3174
Tributylgallium, 3566
Tributylindium, 3567

* Tributyl(phenylethynyl)lead, 3805
† Triethylaluminium, 2548
Triethylantimony, 2569
Triethylgallium, 2558
Triethylindium, 2559
Trimethylaluminium, 1287
Trimethylantimony, 1316
Trimethylbismuthine, 1294
Trimethylgallium, 1301
* Trimethylgermylphosphine, 1328
Trimethylindium, 1303
* Trimethylsilylmethyllithium, 1716
Trimethylthallium, 1317
Tripropylantimony, 3215
Tripropylindium, 3213
* Tripropyllead fulminate, 3357
* Tris(trimethylsilylmethyl)aluminium, 3578
* Tris(trimethylsilylmethyl)indium, 3579
* Trivinylantimony, 2399
* Trivinylbismuth, 2385
* Vinyllithium, 0754

DIALKYLMAGNESIUMS
DIALKYLZINCS
DIPLUMBANES
TRIALKYLALUMINIUMS
TRIALKYLBISMUTHS

See ALKYLALUMINIUM DERIVATIVES, ARYLMETALS, ARYLMETALS, LITHIUM PERALKYLURANATES, TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES

See also METAL ACETYLIDES

ALKYL NITRATES $RONO_2$

Alone, or Lewis acids

1. Boschan, R. *et al., Chem. Rev.*, 1955, **55**, 505
2. Slavinskaya, R. A., *J. Gen. Chem. (USSR)*, 1957, **27**, 844
3. Boschan, R. *et al., J. Org. Chem.*, 1960, **25**, 2012
4. Smith, 1966, Vol. 2, 458
5. Rüst, 1948, 284
6. Urbanski, 1965, Vol. 2, 128
7. Marker, C. D. *et al., Synthesis*, 1977, 485—486
8. Olah, G. A. *et al., Synthesis*, 1978, 452—453
9. Dougherty, V., *J. Haz. Mat.*, 1983, **7**, 247—258
10. Colclough, M. E. *et al., Polym. Adv. Technol.*, 1994, **5**(9), 554

The group of potentially or actually explosive compounds has been reviewed [1]. Ethyl [1], isopropyl, butyl, benzyl and triphenylmethyl nitrates [3] in contact with sulfuric acid [2], tin(IV) chloride [2,3] or boron trifluoride [3] interact violently (after an induction period of up to several hours) with gas evolution. An autocatalytic mechanism was proposed. Although pure alkyl nitrates are stable in storage, traces of oxides of nitrogen sensitise them to decomposition, and may cause explosion on heating or storage at ambient temperature [4].

The most important applications of alkyl nitrates are based on their explosive properties. Methyl and ethyl nitrates are too volatile for widespread use; propyl nitrate has been used as a liquid monopropellant (as also has isopropyl nitrate). Ethylene dinitrate, glyceryl trinitrate and pentaerythritol tetranitrate are widely used as explosives, the two former liquids adsorbed on or blended with other compounds [1]. Poly(nitrate esters) such as poly(glycidyl nitrate) are being studied as energetic binders for explosives and propellants [10]. The nitrate esters of many polyhydroxy compounds (ethylene glycol, glycerol, 1-chloro-2,3-dihydroxypropane, erythritol, mannitol, sugars or cellulose) are all more or less shock-sensitive and will ignite or explode on heating [5]. Glyceryl dinitrate is a slightly less sensitive and powerful explosive than the trinitrate, while the mononitrate explodes at 170°C in a sealed tube [6]. Use of dichloromethane as diluent provides a low-hazard procedure for preparing such esters [7], and in a new method of preparation, the esters are not isolated from solution in acetonitrile [8]. Methods of assessing the relative thermal stabilities of formulated propellant materials containing nitrate esters are reviewed. and a new test to measure isothermal time to auto-ignition is described, together with the Osawa method of predicting the half-life of the substances [9].

Individually indexed compounds are:

Transition metal derivatives

Lur'e, B. A. *et al., Chem. Abs.*, 1981, **95**, 83199

The decomposition rates of several glycol nitrates and glyceryl trinitrate are greatly enhanced by the presence of transition metal oxides or chelates.

2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate, 3460
Benzyl nitrate, 2761
2,2-Bis[(nitrooxy)methyl]propane-1,3-diol dinitrate, 1895
∗ Bis(2-nitratoethyl)nitric amide, 1597
Butyl nitrate, 1656
∗ 1-Chloro-2,3-propylene dinitrate, 1156
2-Cyano-2-propyl nitrate, 1502
∗ 2-Diethylammonioethyl nitrate nitrate, 2566
∗ 2,3-Epoxypropyl nitrate, 1182
† Ethyl nitrate, 0866
Ethylidene dinitrate, 0807
Glyceryl trinitrate, 1192
† Isopropyl nitrate, 1262
Isosorbide dinitrate, 2373
Methyl nitrate, 0456
2,2'-Oxybis(ethyl nitrate), 1594
† Propyl nitrate, 1263
Triphenylmethyl nitrate, 3776
See also Lithium azide: Alkyl nitrates, etc., NITRATING AGENTS (reference 3)
See related ALKENYL NITRATES

ALKYL NITRITES RON:O

1. Sorbe, 1968, 146
2. Rüst, 1948, 285
3. Anon., private comm., 1985

Many alkyl nitrites are thermally unstable and may readily decompose or explode on heating [1]. Methyl nitrite explodes more violently than ethyl nitrite [2]. Lower alkyl nitrites have been known to decompose and burst the container, even in refrigerated storage [3]. Individually indexed compounds are:

† *tert*-Butyl nitrite, 1654
† Butyl nitrite, 1653
Decyl nitrite, 3358
† Ethyl nitrite, 0863
† Isopentyl nitrite, 1990
† Isopropyl nitrite, 1258
† Methyl nitrite, 0454
† Pentyl nitrite, 1992
† Propyl nitrite, 1261

ALKYLNON-METAL HALIDES REX_2, R_2EX, R_2EHX etc.

This class of flammable, air-sensitive and usually pyrophoric compounds includes the groups and the individually indexed compounds:

* Bis(trifluoromethyl)sulfur difluoride, 0644
Chlorodimethylarsine, 0880
* Cyanodimethylarsine, 1195
Dichloromethylarsine, 0423
Dimethylfluoroarsine, 0881
Dimethyliodoarsine, 0882
Ethyliodomethylarsine, 1268
Trifluoromethylsulfur trifluoride, 0362

ALKYLHALOBORANES
ALKYLHALOPHOSPHINES
ALKYLHALOSILANES

ALKYLNON-METAL HYDRIDES REH_2, R_2EH, R_2EH_2, R_3EH

Several of the partially lower-alkylated derivatives of non-metal hydrides are pyrophoric in air. With other gaseous oxidants (halogens, etc.) the reaction may be explosive. The class includes the groups and the individually indexed compounds:

Diethylarsine, 1714
Dimethylarsine, 0933
Ethylmethylarsine, 1289
Methanetellurol, 0488
† Methanethiol, 0487

ALKYLBORANES

ALKYLPHOSPHINES

ALKYLSILANES

See ALKANETHIOLS, ORGANIC BASES

See also the fully alkylated class ALKYLNON-METALS BELOW

ALKYLNON-METALS R_nE

Several of the fully lower-alkylated non-metals are pyrophoric in air, and with other gaseous oxidants (halogens, etc.), reaction may be explosive. The class includes the groups and the individually indexed compounds:

∗ Acetyldimethylarsine, 1623
∗ Allyldimethylarsine, 1977
∗ Bis(dimethylarsinyl) oxide, 1731
∗ Bis(dimethylarsinyl) sulfide, 1732
∗ Bis(dimethylarsinyldiazomethyl)mercury, 2461
∗ Bis(trifluoromethyl) disulfide, 0640
Bis(trifluoromethyl) sulfide, 0639
∗ Dimethylphenylarsine, 2986
∗ Hexaphenylhexaarsane, 3885
∗ Lithium tetramethylborate, 1734
Tetraethyldiarsane, 3081
Tetramethyldiarsane, 1730
Tribenzylarsine, 3816
Triethylarsine, 2552
Trimethylarsine, 1290

ALKYLBORANES

ALKYLPHOSPHINES

ALKYLSILANES

SILYLHYDRAZINES

See also the partially alkylated class ALKYLNON-METAL HYDRIDES

See related TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES

ALKYL PERCHLORATES $ROClO_3$

1. Hofmann, K. A. *et al., Ber.*, 1909, **42**, 4390
2. Meyer, J. *et al., Z. Anorg. Chem.*, 1936, **228**, 341
3. Schumacher, 1960, 214
4. Burton, H. *et al., Analyst*, 1955, **80**, 4
5. Hoffman, D. M., *J. Org. Chem.*, 1971, **36**, 1716
6. Zefirov, N. S. *et al., J. Org. Chem.*, 1985, **50**, 1875

Methyl, ethyl and propyl perchlorates, readily formed from the alcohol and anhydrous perchloric acid, are highly explosive oils, sensitive to shock, heat and friction [1]. Many of the explosions which have occurred on contact of hydroxylic compounds with conc. perchloric acid or anhydrous metal perchlorates are attributable to the formation and decomposition of perchlorate esters [2,3,4]. Safe procedures for preparation of solutions of 14 *sec*-alkyl perchlorates are described. Heated evaporation of solvent caused explosions in all cases [5]. 1-Chloro-2-propyl, *trans*-2-chlorocyclohexyl, 1-chloro-2-propyl, 1,6-hexanediyl, hexyl, and 2-propyl perchlorates, prepared by a new method, are all explosive oils [6].

Individually indexed compounds are:

* 2-Azatricyclo[2.2.1.0^{2,6}]hept-7-yl perchlorate, 2361
Chlorine, : 2-Chloroalkyl aryl sulfides, Lithium perchlorate, 4041
3-Chloro-2-hydroxypropyl perchlorate, 1203
1-Chloro-2-propyl perchlorate, 1202
trans-2-Chlorocyclohexyl perchlorate, 2414
Ethyl perchlorate, 0848
Ethylene diperchlorate, 0791
1,6-Hexanediyl perchlorate, 2464
Hexyl perchlorate, 2515
2(2-Hydroxyethoxy)ethyl perchlorate, 1638
Magnesium perchlorate, : Trimethyl phosphite, 4078
Methoxycarbonylmethyl perchlorate, 1162
Methyl perchlorate, 0435
* Peroxyacetyl perchlorate, 0733
Propyl perchlorate, 1245
2-Propyl perchlorate, 1246
Trichloromethyl perchlorate, 0333
Trifluoromethyl perchlorate, 0320

ALKYLPHOSPHINES RPH_2, R_2PH, R_3P

Many of the lower-alkyl substituted phosphines are pyrophoric; individually indexed compounds are:

* Bis(2-hydroxyethyl)methylphosphine, 2029
* 1,2-Bis(*tert*-butylphosphino)ethane, 3372
* 1,2-Bis-(di-2-propylphosphino)ethane, 3667
* 1,2-Bis(di-*tert*-butylphosphino)ethane, 3770
1,2-Bis(diethylphosphino)ethane, 3373
* Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel, 3831
* Bis(trimethylphosphine)nickel(0)—acetylene complex, 3087
* Di[bis(trifluoromethyl)phosphido]mercury, 1371
* Diethyl ethanephosphonite, 2567
Diethylmethylphosphine, 2030
Diethylphosphine, 1728
* 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclooctane, 2543
Dimethylphenylphosphine, 2998
* Dimethylphenylphosphine oxide, 2997
Dimethylphosphine, 0944
* Dimethyltrimethylsilylphosphine, 2039
* Diphenylphosphine, 3502
1,2-Diphosphinoethane, 0953
* Ethoxytriethyldiphosphinyl oxide, 3088
Ethyldimethylphosphine, 1729

Ethylenebis(dimethylphosphine), 2581
Ethylphosphine, 0945
* 5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole, 2449
Methylphosphine, 0495
* Phenylphosphine, 2353
* Potassium dinitrogentris(trimethylphosphine)cobaltate(1—), 3222
* 2-Tetrahydrofuranylidene(dimethylphenylphosphine-trimethylphosphine)-2,4,6-trimethylphenylnickel perchlorate, 3848
* 2-Tetrahydropyranylidene-bis(dimethylphenylphosphine)-3,4,6-trimethylphenylnickel perchlorate, 3871
* Tetrakis(diethylphosphino)silane, 3727
Tetramethyldiphosphane, 1759
* Tetramethyldiphosphane disulfide, 1760
† Tributylphosphine, 3569
Triethylphosphine, 2568
* Triethylphosphinegold nitrate, 2553
* Triethynylphosphine, 2117
Trifluoromethylphosphine, 0398
Triisopropylphosphine, 3214
Trimethylphosphine, 1315
1-Trimethylsilyloxy-1-trimethylsilylphosphylidine-2,2-dimethylpropane, 3411
* Triphenylphosphine, 3750
* Tris(2,2-dimethylethyl)triphosphirane, 3570
* Tris(2-propylthio)phosphine, 3216
* Tris(trifluoromethyl)phosphine, 1060
See other ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

ALKYLSILANES $RSiH_3$, R_2SiH_2, R_3SiH, R_4Si

Griffiths, S. T. *et al., Combust. Flame*, 1958, **2**, 244—252

Measurements of the autoignition temperatures for several series of mono-, di-, tri- and tetra-alkylsilanes showed that the ease of oxidation decreases with increasing substitution. In this group of easily ignited or pyrophoric compounds, individually indexed compounds are:

* Benzylsilane, 2828
Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane, 2415
* 1,2-Bis(triethylsilyl)hydrazine, 3577
* 1,2-Bis(triethylsilyl)trimethylsilylhydrazine, 3689
* Bis(trimethylsilyl) chromate, 2587
† Bis(trimethylsilyl) oxide, 2597
* *N,N*-Bis(trimethylsilyl)aminoborane, 2608
* *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2611
* Bis(trimethylsilyl)mercury, 2589
* Bis(trimethylsilylmethyl)magnesium, 3093
* 1,2-Bis(tripropylsilyl)hydrazine, 3771
* *N-tert*-Butyl-*N*-trimethylsilylaminoborane, 2873

* *N,N*‘-Di-*tert*-butyl-*N,N*’-bis(trimethylsilyl)diaminophosphene, 3668
† Diethoxydimethylsilane, 2577
† Dimethylaminotrimethylsilane, 2037
* (Dimethylsilylmethyl)trimethyllead, 2601
* Dimethyltrimethylsilylphosphine, 2039
Formyl(triisopropyl)silane, 3364
Hexamethyldisilane, 2604
† Hexamethyldisilazane, 2606
Methylsilane, 0507
Propylsilane, 1327
* Tetrakis(diethylphosphino)silane, 3727
* Tetrakis(trimethylsilyl)diaminodiphosphene, 3582
* Tetramethyldisiloxane, 1777
† Tetramethylsilane, 1764
* 1,1,3,3-Tetramethylsiloxalane, 1768
* Triethoxysilane, 2580
Triethylsilane, 2581
* Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine, 3580
* Trimethylsilylmethyllithium, 1716
* *N*-Trimethylsilyl-*N*-trimethylsilyloxyacetoacetamide, 3369
* Tris(2-pylthio)silane, 3216
* Tris(trimethylsilyl)aluminium, 3221
* *N,N,N*’-Tris(trimethylsilyl)diaminophosphine, 3226
* Tris(trimethylsilylmethyl)aluminium, 3578
* Tris(trimethylsilylmethyl)indium, 3579
* Tris(trimethylsilyl)phosphine, 3223
Tris(trimethylsilyl)silane, 3225
See other ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

ALKYL TRIALKYLLEAD PEROXIDES $ROOPbR'_3$

Houben-Weyl, 1975, Vol. 13.3, 111
These unstable compounds may decompose very violently on heating.
See other ORGANOMETALLIC PEROXIDES

ALKYNES R—C≡C—

† Acetylene, 0682
† 1,3-Butadiyne, 1381
* 4,4’-(Butadiyne-1,4-diyl)bis(2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl), 3832
† Buten-3-yne, 1419
† 1-Butyne, 1477
† 2-Butyne, 1478
1,7,13-Cyclooctadecatriene-3,5,9,11,15,17-hexayne, 3734
1,7,13,19-Cyclotetracosatetraene-3,5,9,11,15,17,21,23-octayne, 3837
11,12-Diethynyl-9,10-dihydro-9,10-ethenoanthracene, 3786
1,4-Diethynylbenzene, 3235

3,3-Dimethyl-1-butyne, 2402
1,8-Diphenyloctatetrayne, 3782
Hepta-1,3,5-triyne, 2637
1-Heptene-4,6-diyne, 2703
† 1-Heptyne, 2834
† 1,5-Hexadien-3-yne, 2284
1,3-Hexadien-5-yne, 2283
2,4-Hexadiyne, 2286
1,5-Hexadiyne, 2285
1,3,5-Hexatriyne, 2067
3-Hexyne, 2409
† 1-Hexyne, 2408
† 2-Methyl-1-buten-3-yne, 1852
† 3-Methyl-1-butyne, 1888
3-Nitrophenylacetylene, 2900
∗ 1,3,7-Octatrien-5-yne, 2938
† 2-Octyne, 3018
† 3-Octyne, 3019
† 4-Octyne, 3020
† 1-Octyne, 3017
† 1-Pentyne, 1892
† 2-Pentyne, 1893
Phenylacetylene, 2907
∗ Poly(butadiyne), 1382
† Propyne, 1122
See Nitrogen oxide: Dienes, etc.
Oxides of Nitrogen
See ACYL AZIDES
See also ROTANES
See other ACETYLENIC COMPOUNDS

ALLOYS (INTERMETALLIC COMPOUNDS)

Individually indexed alloys or intermetallic compounds are:
Aluminium amalgam, 0051
Aluminium—copper—zinc alloy, 0050
Aluminium—lanthanum—nickel alloy, 0080
Aluminium—lithium alloy, 0052
Aluminium—magnesium alloy, 0053
Aluminium—nickel alloys, 0055
Aluminium—titanium alloys, 0056
Copper—zinc alloys, 4262
Ferromanganese, 4383
Ferrotitanium, 4385
Lanthanum—nickel alloy, 4673

Lead—tin alloys, 4877
Lead—zirconium alloys, 4878
Lithium—magnesium alloy, 4676
Lithium—tin alloys, 4677
Plutonium bismuthide, 0231
Potassium antimonide, 4668
Potassium—sodium alloy, 4641
Silicon—zirconium alloys, 4904
Silver—aluminium alloy, 0002
* Silvered copper, 0003
Sodium germanide, 4412
Sodium—antimony alloy, 4791
Sodium—zinc alloy, 4792
Titanium—zirconium alloys, 4915
See also LANTHANIDE—TRANSITION METAL ALLOY HYDRIDES

ALLYL COMPOUNDS **$H_2C=CHCH_2$—**

Several allyl compounds are notable for their high flammability and reactivity. There are group entries and individually indexed compounds.

Individually indexed compounds are:

Allyl 4-toluenesulfonate, 3309
† Allyl acetate, 1906
Allyl benzenesulfonate, 3149
† Allyl formate, 1521
Allyl hydroperoxide, 1222
* Allyl isothiocyanate, 1467
Allyl phosphorodichloridite, 1165
† Allyl vinyl ether, 1898
* Allyldimethylarsine, 1977
Allyllithium, 1173
Allylmercury(II) iodide, 1169
1-Allyloxy-2,3-epoxypropane, 2428
N-Allylthiourea, 1595
† 3-Aminopropene, 1250
3-Azidopropene, 1184
† 3-Bromo-1-propene, 1149
† 1-Bromo-2-butene, 1543
1-Chloro-4-(2-nitrophenyl)-2-butene, 3264
N-Chloroallylamine, 1198
† 3-Chloropropene, 1154
† 3-Cyanopropene, 1461
* Di-2-butenylcadmium, 3022
† Diallyl ether, 2425
Diallyl peroxydicarbonate, 2984
Diallyl phosphite, 2450

Diallyl sulfate, 2437
Diallyl sulfide, 2441
† Diallylamine, 2444
† 3,3-Dimethoxypropene, 1962
1-Heptene-4,6-diyne, 2703
† 3-Iodopropene, 1170
† 2-Propen-1-ol, 1219
† 2-Propene-1-thiol, 1235
Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3499
Tetraallyl-2-tetrazene, 3539
* Tetraallyluranium, 3542
Triallyl phosphate, 3178
* Triallylchromium, 3174
2,4,6-Triallyloxy-1,3,5-triazine, 3524
3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2843

ALLYL TRIFLUOROMETHANESULFONATES
ALLYLIC HYDROPEROXIDES
See other PEROXIDISABLE COMPOUNDS

ALLYLIC HYDROPEROXIDES —CH=CH—CH(OOH)—

Preparative hazard

Frimer, A. A., *J. Org. Chem.*, 1977, **42**, 3194—3196, footnote 7

A new method of preparation involves interaction of allylic halides in solvents with 98% hydrogen peroxide in presence of silver ion and base at ambient temperature under argon. The reactions must be run in the dark to prevent precipitation of metallic silver, which will catalyse decomposition of the hydroperoxide or excess hydrogen peroxide. In an experiment not run in the dark, the hydroperoxide from 3-chlorocyclohexene ignited spontaneously after isolation and concentration.

See other ALKYL HYDROPEROXIDES

ALLYL TRIFLUOROMETHANESULFONATES $RCH=CR'CH_2OSO_2CF_3$

Alone, or Aprotic solvents

Vedejs, E. *et al., J. Org. Chem.*, 1977, **42**, 3109—3113

Trifluoromethanesulfonate esters (‘triflates’) of allyl alcohol and its derivatives are very reactive and undiluted samples must be stored in vented containers at —78°C. A chilled sample of allyl triflate in a sealed ampoule exploded on being allowed to warm to ambient temperature. The esters react violently with aprotic solvents such as DMF or DMSO. Individually indexed compounds are:

2-Chloro-2-propenyl trifluoromethanesulfonate, 1422
3-Methoxycarbonylpropen-2-yl trifluoromethanesulfonate, 2346
Prop-2-enyl trifluoromethanesulfonate, 1457
3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2843

See other ALLYL COMPOUNDS, SULFUR ESTERS

AMINATION INCIDENTS

Gordon, M. D., *Adv. Instrum.*, 1988, **43**(1), 75—81

Kinetic simulation methods are used as advisory controls in potentially thermally hazardous batch amination reactions of nitroaromatic compounds. Time—temperature process data are fed as input to a kinetic simulation computer program which calculates conversions, heat release and pressure profiles. Results are compared continuously on-line with measured batch data to detect any deviations from normal operating conditions.

Incidents involving reactions with either ammonia or organic amines (sometimes only in catalytic proportions) may be found under the entries:

Benzenediazonium-2-carboxylate, : Aniline, or Isocyanides, 2655
1-Chloro-2,4-dinitrobenzene, : Ammonia, 2091
4-Chloroacetophenone, : Dimethylamine, 2924
2-Chloronitrobenzene, : Ammonia, 2134

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

AMINE OXIDES $RR'R'N \rightarrow O$

Editor's comments

Several tertiary amine oxides are reported as exploding, usually on heating well above 100°C. Paradoxically, these tend to be the more stable members of the group, those which for conformational reasons cannot undergo the Cope rearrangement. As this class of compound is of growing importance, more incidents can be expected, possibly including violent decomposition of the alkylhydroxylamine products of the Cope reaction as well as the apparently radical branched chain, higher temperature decomposition which accounts for present reports. Early workers developed spot tests for amine oxides which later study has shown they do not perform but hydrogen peroxide does; since amine oxides tenaciously hold water as hydrates it must be suspected that they can also form hydrogen peroxidates if made using excess hydrogen peroxide. These will be more dangerous than the amine oxide itself.

See also CRYSTALLINE HYDROGEN PEROXIDATES
See other N—O COMPOUNDS, N-OXIDES

AMINIUM IODATES AND PERIODATES $RN^+H_3\ IO_3^-$, $RN^+H_3\ IO_4^-$

Fogel'zang, A. E. *et al., Chem. Abs.*, 1975, **83**, 8849

Combustion rates of the periodate salts of amines exceed those of the corresponding iodate salts.

See OXOSALTS OF NITROGENOUS BASES, PERCHLORATE SALTS OF NITROGENOUS BASES

AMINIUM NITRATES $RN^+H_3\ NO_3^-$

Anon., *Chem. Hazards Ind.*, 1992, (Jul.) 1218

Many nitrate salts of amines are highly crystalline, which encourages their use to isolate amines; they are also often explosive, which does not. An industrial explosion consequent upon inadvertent isolation of such in part of a production plant, with subsequent overheating is reported [1].

See also Nitric acid: Alkylamines
See also OXOSALTS OF NITROGENOUS BASES

AMINIUM PERCHLORATES $RN^+H_3\ ClO_4^-$

Datta, R. L. *et al., J. Chem. Soc.*, 1919, **115**, 1006—1010

Many perchlorate salts of amines explode in the range 215—310°C, and some on impact at ambient temperature. Individually indexed compounds are to be found in the group entries:

PERCHLORATE SALTS OF NITROGENOUS BASES
POLY(AMINIUM) PERCHLORATES

AMINOMETHOXY COMPOUNDS H_2N-Alkyl-OMe, H_2N-Aryl-OMe

Several members of this group show considerable energies of decomposition by DSC examination.

Individually indexed compounds are :

2-Bromo-3,5-dimethoxyaniline, 2969
3-Chloro-4-methoxyaniline, 2791
3,5-Dimethoxyaniline, 2994
4-Methoxy-1,3-phenylenediamine, 2822
2-Methoxy-5-nitroaniline, 2798
4-Methoxyaniline, 2814
3-Methoxyaniline, 2813
2-Methoxyaniline, 2812
* 2-Methoxyanilinium nitrate, 2825
3-Methoxybenzylamine, 2992
† 2-Methoxyethylamine, 1308
* 1-(4-Methoxyphenyl)-3-methyltriazene, 2995
3-Methoxypropylamine, 1724

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)
See other ORGANIC BASES

AMMINECHROMIUM PEROXOCOMPLEXES $H_3N \rightarrow Cr—OO—$

This group of compounds, previously described as ‘amine perchromates’, is characterised by the presence of basic nitrogen and peroxo ligands within the same coordination sphere. This creates a high tendency towards explosive decomposition, which sometimes apparently occurs spontaneously. Individually indexed compounds are:

Ammine-1,2-diaminoethanediperoxochromium(IV), 0964
Aqua-1,2-diaminoethanediperoxochromium(IV), 0961
Aqua-1,2-diaminopropanediperoxochromium(IV) dihydrate, 1332
Bis(2-aminoethyl)aminediperoxochromium(IV), 1770
1,2-Diamino-2-methylpropaneoxodiperoxochromium(VI), 1740
Dianilineoxodiperoxochromium(VI), 3517
* (Dimethyl ether)oxodiperoxochromium(VI), 0900
* Hexamethylenetetrammonium tetraperoxochromate(V)?, 3773
Hydrogen cyanide, 0379
* Oxodiperoxodi(pyridine *N*-oxide)molybdenum, 3273
* Oxodiperoxodi(pyridine *N*-oxide)tungsten, 3277
Oxodiperoxodipyridinechromium(VI), 3268

Oxodiperoxodiquinolinechromium(VI), 3742

* Oxodiperoxomolybdenum—hexamethylphosphoramide, 4713

Oxodiperoxopyridinechromium *N*-oxide, 1838

* Oxodiperoxy(pyridine)(1,3-dimethyl-2,4,5,6-tetrahydro-2-1*H*)-pyrimidinone)molybdenum, 3404

* μ-Peroxobis[ammine(2,2′,2′′-triaminotriethylamine)cobalt(III)](4+) perchlorate, 3585

* Potassium pentacyanodiperoxochromate(5—), 1804

Triamminediperoxochromium(IV), 4225

* Triphenylphosphine oxide-oxodiperoxochromium(VI), 3746

See PEROXOCHROMIUM COMPOUNDS

See related AMMINEMETAL OXOSALTS

AMMINEMETAL AZIDES $H_3N{\rightarrow}Co{-}N_3$

1. Joyner, T. B., *Chem. Abs.*, 1970, **72**, 113377
2. Narang, K. K. *et al., Synth. React. Inorg. Met.-Org. Chem.*, 1996, **26**(4), 573
3. Divan, R. *et al., Chem. Abs.*, 1999, **131**, 136683f

The explosive properties of a series of 5 amminecobalt(III) azides were examined in detail. Compounds were hexaamminecobalt triazide, pentaammineazidocobalt diazide, *cis*- and *trans*-tetraamminediazidocobalt azide, triamminecobalt triazide [1]. A variety of hydrazine complexed azides and chloroazides of divalent metals have been prepared. Those of iron, manganese and copper could not be isolated; cobalt, nickel, cadmium and zinc gave products stable at room temperature but more or less explosive on heating [2]. Some polyammine azido-metal nitrates of Cr, Ni and Cu were found to be explosively photosensitive. Replacement of ammonia by triethanolamine gave compounds smoothly photodecomposing [3].

See Cobalt(II) azide

AMMINE METAL NITRATES

See AZIDE COMPLEXES OF COBALT(III)

See related METAL AZIDE HALIDES, METAL AZIDES

AMMINEMETAL HALIDES $H_3N{\rightarrow}M^+\ X^-$

Author’s comment.

Although free from the formally oxidising anions present in the two groups below, a few of these compounds show instability. These are:

cis-Bis(trimethylsilylamino)tellurium tetrafluoride, 2611

Pentaamminechlororuthenium chloride, 4131

N,N,N,′N′-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) bromide, 3219

N,N,N′,N′-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) iodide, 3220

See AMMINEMETAL OXOSALTS

AMMINEMETAL NITRATES $H_3N{\rightarrow}M^+\ NO_3^-$

Author’s comment.

Compounds in this group show explosive instability tending towards that of the perchlorate analogues in the entry following. Individual nitrates are:

Bis(1-methylbenzotriazole)cobalt(II) nitrate, 3645

Bis(2-aminoethyl)aminesilver nitrate, 1767
Diamminenitratocobalt(II) nitrate, 4196
Diamminepalladium(II) nitrate, 4557
Hexaamminechromium(III) nitrate, 4228
* Hexaamminecobalt(III) hexanitrocobaltate(3—), 4213
Hexaamminecobalt(III) nitrate, 4204
* Hexahydroxylaminecobalt(III) nitrate, 4205
* Hexaureachromium(III) nitrate, 2619
Pentaamminenitratocobalt(III) nitrate, 4201
Pentaamminenitrochromium(III) nitrate, 4227
Tetraamminecopper(II) nitrate, 4270
Tetraamminehydroxynitratoplatinum(IV) nitrate, 4589
Tetraamminenickel(II) nitrate, 4582
Tetraamminepalladium(II) nitrate, 4583
Tetraammineplatinum(II) nitrate, 4585
Triamminenitratoplatinum(II) nitrate, 4577
1,2,4-Triazolo[4,3-*a*]pyridine—silver nitrate, 2263
* Triethylphosphinegold nitrate, 2553
Tris(1,2-diaminoethane)cobalt(III) nitrate, 2618
Tris(2,3-diaminobutane)nickel(II) nitrate, 3583
See AMMINEMETAL OXOSALTS (next below)
See also AMMINEMETAL AZIDES

AMMINEMETAL OXOSALTS $H_3N{\rightarrow}M^+ \; EO_n^-$

1. Mellor, 1941, Vol. 2, 341—364, 404
2. Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 375
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Metal compounds containing both coordinated ammonia, hydrazine, hydroxylamine or similar nitrogenous donors, and coordinated or ionic perchlorate, chlorate, nitrate, nitrite, nitro, permanganate or other oxidising groups will decompose violently under various conditions of impact, friction or heat [1,2]. From tabulated data for 17 such compounds of Co and Cr, it is considered that oxygenated *N*-coordinated compounds, (particularly those which are oxygen balanced) cover a wide range of explosive types;

many may explode powerfully with little or no provocation, and should be considered extremely dangerous, as some are sensitive enough to propagate explosion under water. The same considerations may be expected to apply to ammines of silver, gold, cadmium, lead and zinc which contain oxidising radicals [2]. The topic has been reviewed [3] and possible hazards in published student preparations were emphasised [4]. Some of the derivatives of metal biguanide and guanylurea complexes [5] are of this group.

Unexpected uniformities observed in the impact-sensitivities of a group of 22 amminecobalt oxosalts are related to kinetic factors during the initiation process [6]. A series of ammine derivatives of cadmium, cobalt, copper, mercury, nickel, platinum and zinc with (mainly) iodate anions was prepared and evaluated as explosives [7]. Earlier, ammine and hydrazine derivatives of cadmium, cobalt, copper and nickel with chlorate or perchlorate anions had been evaluated as detonators. Dihydrazinecopper(II) chlorate had exploded when dried at ambient temperature [8].

A series of pyrazole complexes which decompose explosively above 200°C is notable in that the anion is sulfate, rather than the more obvious oxidant species usually present. The compounds are manganese sulfate complexed with 4 mol of pyrazole or 3-methylpyrazole, and cadmium or zinc sulfates complexed with 4 and 3 mol of 3-methylpyrazole, respectively [9]. Around 100°C the hexaammine diperchlorates of copper and zinc decompose to the tetraammines, and those of cadmium, cobalt, manganese and nickel to the diammines. Around 220°C all these lower ammines decompose explosively to the metal oxides (or the chloride for cadmium) [10]. The use of a soft polythene rod is recommended to reduce the possibility of explosions when handling perchlorate and similar salts on sintered filters [11]. Ignition temperatures and burning velocities of the hydrazine complexes of the picrates, styphnates or nitrates of cobalt, copper or nickel were 100°C lower, and an order of magnitude higher, respectively, than those of the corresponding ammine complexes [12]. A 3 g sample of the perchlorate salt of a polyaminerhodium complex exploded with great violence in a rotary evaporator flask heated in a water bath [13]. A series of tetrammine metal(II) nitrates (Pt, Pd, Cu, Ni) were all found to be practically and legally classifiable as sensitive explosives. It was sugggested that heavy metal contamination was responsible for the ammonium nitrate/sulphate explosion at Oppau [14].

Individually indexed compounds in this large group are:

Ammonium hexanitrocobaltate(3—), 4200
Aquafluorobis(1,10-phenanthroline)chromium(III) perchlorate, 3840
* Basic trihydrazinecadmium perchlorate, 3945
(Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2610
* 2,2′-Bipyridine *N,N*′-dioxide-dicarbonylrhodium(I) perchlorate, 3448
4,4′-Bipyridyl-bis(pentaammineruthenium(III) perchlorate), 3379
2,2′-Bipyridyldichloropalladium(IV) perchlorate, 3249
* Bis *O,N*[(*N*′-pent-2-en-2-oxy-4-ylidene)-*N,S*-dimethyldithiocarbazate]copper(II) perchlorate, 3712
Bis(1,2-diaminoethane)diaquacobalt(III) perchlorate, 1787
Bis(1,2-diaminoethane)dichlorocobalt(III) chlorate, 1780
Bis(1,2-diaminoethane)dichlorocobalt(III) perchlorate, 1781
cis-Bis(1,2-diaminoethane)dinitrocobalt(III) iodate, 1782

Bis(1,2-diaminoethane)dinitrocobalt(III) perchlorate, 1778
Bis(1,2-diaminoethane)hydroxooxorhenium(V) perchlorate, 1785
Bis(1,2-diaminopropane)-*cis*-dichlorochromium(III) perchlorate, 2609
* Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3785
Bis(2-aminoethyl)aminesilver nitrate, 1767
* Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3827
N,N′-Bis(3-aminopropyl)-1,4-diazacycloheptanenickel(II) perchlorate, 3409
Bis(diethylenetriamine)cobalt(III) perchlorate, 3100
* 1,2-Bis(diphenylphosphino)ethanepalladium(II) perchlorate, 3858
Bis(hydrazine)diperchloratochromium(III) perchlorate, 4122
Bis(hydrazine)nickel perchlorate, 4063
* Bis(hydrazine)tin(II) chloride, 4064
* Bis(hydroxylamine)zinc chloride, 4061
Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate, 3847
* Bis(tetramethyldiphosphane disulfide)cadmium perchlorate, 3096
* Carbonyl-bis(triphenylphosphine)iridium—silver diperchlorate, 3892
* 5-*p*-Chlorophenyl-2,2-dimethyl-3-hexanone, 3657
Copper(II) perchlorate, : *N*-(2-Pyridyl)acylacetamides, 4051
Copper(II) perchlorate, : Polyfunctional amines, 4051
2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate, 0970
* 1,5-Cyclooctadiene-bis(4-chloropyridine *N*-oxide)rhodium(I) perchlorate, 3755
* Di[*N,N′*-Ethylenebis(2-oxidoacetophenoneiminato)copper(II)] oxovanadium(IV) diperchlorate, 3887
* Di[tris(1,2-diaminoethanechromium(III)] triperoxodisulfate, 3587
* Di[tris-1,2-diaminoethanecobalt(III)] triperoxodisulfate, 3586
trans-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) perchlorate, 3377
Diamminenitratocobalt(II) nitrate, 4196
Diamminepalladium(II) nitrate, 4557
Diamminepalladium(II) nitrite, 4554
cis-Diammineplatinum(II) nitrite, 4555
Diamminesilver permanganate, 0018
* Dicarbonyl(phenanthroline *N*-oxide)rhodium(I) perchlorate, 3619
* Dicarbonylpyrazinerhodium(I) perchlorate, 2140
* *trans*-Dichlorobis[1,2-phenylenebis(dimethylarsine)]palladium(IV) diperchlorate, 3802
Dihydrazinecobalt(II) chlorate, 4043
Dihydrazinemanganese(II) nitrate, 4565
Dihydrazinesilver nitrate, 0019
6,6′-Dihydrazino-2,2′-bipyridylnickel(II) perchlorate, 3297
Dipyridinesilver(I) perchlorate, 3261
Hexaamminechromium(III) nitrate, 4228
Hexaamminechromium(III) perchlorate, 4123
Hexaamminecobalt(III) chlorate, 4119
Hexaamminecobalt(III) hexanitrocobaltate(3—), 4213
Hexaamminecobalt(III) iodate, 4202
Hexaamminecobalt(III) nitrate, 4204

Hexaamminecobalt(III) perchlorate, 4120
Hexaamminecobalt(III) permanganate, 4203
Hexaamminenickel chlorate, 4068
Hexaamminenickel perchlorate, 4069
Hexahydroxylaminecobalt(III) nitrate, 4205
* Hexakis(pyridine)iron(II) tridecacarbonyltetraferrate(2—), 3900
* Hexamethylenetetrammonium tetraperoxochromate(V)?, 3773
* Hexaureachromium(III) nitrate, 2619
* Hexaureagallium(III) perchlorate, 2616
4-[2-(4-Hydrazino-1-phthalazinyl)hydrazino]-4-methyl-2-pentanone(4-hydrazino-1-phthalazinyl)hydrazonedinickel(II) tetraperchlorate, 3830
Isonicotinamidepentaammineruthenium(II) perchlorate, 2614
* Mercury(II) perchlorate, 4072
Octaammine-μ-hydroxy[-μ-(superoxido-*O,O′*)]dirhodium(4+) nitrate, 4592
Octammine-μ-hydroxy[μ-(peroxy-*O:O′*)]dirhodium(3+) perchlorate, 4132
* Oxybis(*N,N*-dimethylacetamidetriphenylstibonium) perchlorate, 3905
Pentaammineaquacobalt(III) chlorate, 4118
Pentaamminechlorocobalt(III) perchlorate, 4117
Pentaamminedinitrogenosmium(II) perchlorate, 4066
Pentaamminenitratocobalt(III) nitrate, 4201
Pentaamminenitrochromium(III) nitrate, 4227
Pentaamminephosphinatochromium(III) perchlorate, 4047
Pentaamminephosphinatocobalt(III) perchlorate, 4044
Pentaamminepyrazineruthenium(II) perchlorate, 1786
Pentaamminepyridineruthenium(II) perchlorate, 2042
Pentaamminethiocyanatocobalt(III) perchlorate, 0516
Pentaamminethiocyanatoruthenium(III) perchlorate, 0517
* Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3772
* μ-Peroxobis[ammine(2,2′,2′′-triaminotriethylamine)cobalt(III)](4+) perchlorate, 3585
* Tetra(3-aminopropanethiolato)trimercury perchlorate, 3576
* Tetraacrylonitrilecopper(I) perchlorate, 3504
Tetraammine-2,3-butanediimineruthenium(III) perchlorate, 1788
Tetraamminebis(dinitrogen)osmium(II) perchlorate, 4065
Tetraamminecadmium permanganate, 3950
Tetraamminecopper(II) bromate, 0263
Tetraamminecopper(II) nitrate, 4270
Tetraamminecopper(II) nitrite, 4269
Tetraamminecopper(II) sulfate, 4268
Tetraamminedithiocyanatocobalt(III) perchlorate, 0965
Tetraamminehydroxynitratoplatinum(IV) nitrate, 4589
Tetraamminepalladium(II) nitrate, 4583
Tetraamminezinc peroxodisulfate, 4581
1,4,8,11-Tetraazacyclotetradecanenickel(II) perchlorate, 3370
Tetrakis(3-methylpyrazole)cadmium sulfate, 3710
Tetrakis(3-methylpyrazole)manganese(II) sulfate, 3711

Tetrakis(4-*N*-methylpyridinio)porphinecobalt(III)(5+) perchlorate, 3902
Tetrakis(4-*N*-methylpyridinio)porphineiron(III)(5+) perchlorate, 3903
Tetrakis(pyrazole)manganese(II) sulfate, 3532
* Tetrakis(thiourea)manganese(II) perchlorate, 1779
Tetrakis(μ_3-2-amino-2-methylpropanolato)tetrakis(μ_2-2.amino-2-methylpropanolato)hexacopper(II) perchlorate, 3877
Triamminenitratoplatinum(II) nitrate, 4577
Triamminetrinitrocobalt(III), 4198
* 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate, 3179
* 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, 3180
1,2,4-Triazolo[4,3-*a*]pyridine—silver nitrate, 2263
Trihydrazinealuminium perchlorate, 0064
Trihydrazinecadmium chlorate, 3944
Trihydrazinecobalt(II) nitrate, 4199
Trihydrazinenickel(II) nitrate, 4587
Tris(1,10-phenanthroline)cobalt(III) perchlorate, 3884
Tris(1,10-phenanthroline)ruthenium(II) perchlorate, 3883
Tris(1,2-diaminoethane)chromium(III) perchlorate, 2615
Tris(1,2-diaminoethane)cobalt(III) nitrate, 2618
Tris(1,2-diaminoethane)ruthenium(III) perchlorate, 2617
Tris(2,2′-bipyridine)chromium(II) perchlorate, 3868
Tris(2,2′-bipyridine)silver(II) perchlorate, 3867
Tris(2,3-diaminobutane)nickel(II) nitrate, 3583
Tris(3-methylpyrazole)zinc sulfate, 3534
Tris(4-methoxy-2,2′bipyridine)ruthenium(II) perchlorate, 3880
* 1,4,7-Trithia[7]ferrocenophene—acetonitrilecopper(I) perchlorate, 3704

CLATHROCHELATED METAL PERCHLORATES
HYDRAZINEMETAL NITRATES
METAL PERCHLORATES: Organic ligands
POLYAZACAGED METAL PERCHLORATES
SOLVATED OXOSALT INCIDENTS
URANYL MACROCYCLIC PERCHLORATE LIGANDS
See AMMINECHROMIUM PEROXOCOMPLEXES, [14] DIENE-N_4 COMPLEXES

ANNULENES

Polyacetylenes intended as intermediates in synthesis of, especially, [18] annulene have been the major growth area in academic explosion from the 5th to the 6th edition of this handbook. No injuries and negligible damage have resulted, doubtless as much due to the care of the researchers as the often limited power of the compounds. Annulenes do not yet seem to have resulted even when they should be the initial decomposition product, implying that they will not be very stable themselves. Related compounds are now deliberately being caused to explode in hopes of preparing carbon nanostructures.

ACETYLENIC COMPOUNDS
See also ROTANES

APROTIC SOLVENTS

1. Buckley, A., *J. Chem. Educ.*, 1965, **42**, 674
2. Banthorpe, D. V., *Nature*, 1967, **215**, 1296

Many aprotic (non-hydroxylic) solvents are not inert towards other reagents and care is necessary when using untried combinations of solvents and reagents for the first time. A further potential hazard which should be considered is that some aprotic solvents, notably dimethyl sulfoxide [1] and dimethylformamide [2], as well as having dramatic effects upon reaction rates, may greatly promote the toxic properties of solutes because of their unique ability to penetrate synthetic rubber protective gloves and the skin. Butyl rubber gloves are reputed to be more satisfactory than other types. The ether and cyclic ether solvents are also subject to peroxidation in storage.

Individually indexed compounds are:
† Dimethyl sulfoxide, 0917
N,N-Dimethylacetamide, 1651
Dimethylformamide, 1255
† 1,4-Dioxane, 1612
† Furan, 1435
N-Methylformamide, 0862
† Tetrahydrofuran, 1607
Tetrahydrothiophene-1,1-dioxide, 1617

AQUA REGIA **$NOCl.Cl_2.2H_2O$**

Fawcett, H. H., *Chem. Eng. News*, 1955, **33**, 897, 1406, 1622, 1844

Aqua regia (nitric and hydrochloric acids, 1:4 by vol., a powerful oxidant), which had been used for cleaning purposes, was stored in screw-capped winchesters. Internal pressure developed overnight, one bottle being shattered. Aqua regia decomposes with evolution of gas and should not be stored in tightly closed bottles (and preferably not at all).

See Nitric acid: Alcohols

Sodium

Chatt, J. *Biographical Memoirs*, Royal Society, 1996, 98.

Addition of a piece of sodium to aqua regia produces spectacular sparks.

AQUA REGIA, 4790

ARENECYCLOPENTADIENYLIRON(II) PICRATES **$RC_6H_5Fe^{2+}C_5H_5.2C_6H_2(NO_2)_3O^-$**

Federman Neto, A. *et al., An. Acad. Bras. Cienc.*, 1982, **54**, 331—333

The products of condensing substituted benzenes and ferrocene with $Al/AlCl_3$ were isolated as the picrate salts, which were light-sensitive and explosive.

See other PICRATES

ARENEDIAZO ARYL SULFIDES **ArN=NSAr**

See DIAZONIUM SULFIDES AND DERIVATIVES

ARENEDIAZOATES $ArN{=}NOR$

Houben-Weyl, 1965, Vol. 10.3, 563—564

Alkyl and aryl arenediazoates ('diazoethers') are generally unstable and even explosive compounds. They are produced by interaction of alcohols with (explosive) bis(arenediazo) oxides, or of *p*-blocked phenols with diazonium salts. The thio analogues are similar. Individually indexed compounds are:

Methyl 2-nitrobenzenediazoate, 2778
Methyl 4-bromobenzenediazoate, 2733
Methyl benzenediazoate, 2795
2-(4-Nitrophenoxyazo)benzoic acid, 3595
* Potassium 1-phenylethanediazoate, 2959
* Potassium methanediazoate, 0448
See related DIAZONIUM SULFIDES AND DERIVATIVES

ARENEDIAZONIUM OXIDES $N_2^+ArO^-$

This group of internal diazonium salts (previously named diazooxides) contains those which are, like many other internal diazonium salts, explosively unstable and shock-sensitive materials. A diazo-2 or 4-oxocyclohexadiene structure is another possible representation and nomenclature.

Other early names of the 1,2-diazonium oxides were based on the benzoxadiazole cyclised structure. For a long time it was doubted that 1,2,3-Benzoxadiazoles had existence, outside the speculative mathematics of theoretical chemists, but more recent researches suggest photochemical equilibrium with the diazonium form and possible predominance in non-polar solvents. Equilibrium implies similar explosive powers though it is possible that sensitivities differ.

Individually indexed compounds are:

Benzenediazonium-4-oxide, 2182
5-Benzoylbenzenediazonium-2-oxide, 3591
3-Bromo-2,7-dinitrobenzo[*b*]thiophene-5-diazonium-4-oxide, 2878
4-Chloro-2,5-dinitrobenzenediazonium 6-oxide, 2059
5-Diazoniotetrazolide, 0545
3,6-Difluoro-2-nitrobenzenediazonium 4-oxide, 2061
3,4-Difluoro-2-nitrobenzenediazonium 6-oxide, 2060
3,5-Dinitro-2-methylbenzenediazonium-4-oxide, 2662
3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide, 2083
3,5-Dinitro-6-methylbenzenediazonium-2-oxide, 2663
4,6-Dinitrobenzenediazonium 2-oxide, 2081
3,5-Dinitrobenzenediazonium 2-oxide, 2080
2,3,5-Trinitrobenzenediazonium-4-oxide, 2065
See also Benzenediazonium-4-sulfonate
See DIAZONIUM CARBOXYLATES

ARTIFICIAL FINGERNAILS

Vanover, W. G. *et al., J. Chem. Ed.*, 1999, **76**(11), 1521

These are highly combustible and easily ignited. The natural reaction to a combusting claw, shaking the hand violently, is likely to distribute burning polymer droplets broadcast. Not advised in laboratories.

ARYL CHLOROFORMATES (ARYL CARBONOCHLORIDATES) ArOCO.Cl

Water

Muir, G. D., private comm., 1968

During the preparation of aryl chloroformates, it is essential to keep the reaction mixture really cold during water washing to prevent vigorous decomposition. Phenyl and naphthyl chloroformates may be distilled, but benzyl chloroformate is too thermally unstable.

2-ARYLIDENEAMINO-4,6-DINITROPHENOL SALTS $(ArCH{=}NC_6H_2(NO_2)_2O)_2M$

1. Srivastan, R. S. *et al., Def. Sci. J.*, 1979, **29**, 91—96
2. Srivastan, R. S., *Def. Sci. J.*, 1982, **32**, 219—223

The 4′-dimethylaminobenzylidene derivatives form explosive cadmium, mercury and zinc salts [1], and the 4′-nitro analogue forms explosive cadmium, cobalt, copper, iron, mercury, nickel and zinc salts of limited thermal stability [2]. All are constituted with a 1:2 metal:ligand ratio.

See 2-Benzylideneamino-4,6-dinitrophenol

ARYLMETALS ArM

This reactive group includes the individually indexed compounds:

* 3-Benzocyclobutenylpotassium, 2899
* Bis(cyclopentadienyl)phenylvanadium, 3698
* Bis(η-benzene)chromium(0), 3505
* Bis(η-benzene)iron(0), 3506
* Bis(η-benzene)molybdenum(0), 3508
Dicumenechromium(0), 3761
1,3-Dilithiobenzene, 2171
1,4-Dilithiobenzene, 2172
* Diphenyldistibene, 3494
Diphenylmagnesium, 3476
Diphenylmercury, 3473
Diphenyltin, 3496
* Lithium diphenylhydridotungstate(2—), 3497
* Lithium hexaphenyltungstate(2—), 3886
Naphthylsodium, 3247
2-,3- or 4-Tolylcopper, 2739
Phenylgold, 2214
Phenyllithium, 2252
Phenylsilver, 2210
Phenylsodium, 2280
* Phenylvanadium(V) dichloride oxide, 2239
Tetraphenyllead, 3844

Triphenylaluminium, 3743
Triphenylchromium tetrahydrofuranate, 3745
* Triphenyllead nitrate, 3747
See also ALKYLMETALS

(ARYLSULFONYLIMINOIODO)BENZENES **$ArSO_2N{=}I\text{-}Ph$**

Meprathu, B. V. *et al., Tetrahedron Lett.*, 1999, **40**(30), 5459
Three heterocyclic examples of this class, ArSO2N=IPh were prepared, Ar being 2-pyridyl, 1-oxo-2-pyridyl and 1-methyl-2-imidazolyl. They decompose explosively on melting.
See other IODINE COMPOUNDS

ARYLTHALLIC ACETATE PERCHLORATES **$ArTl(OAc)ClO_4$**

See Perchloric acid: Ethylbenzene, etc.

1-ARYL-1-VINYLLITHIUM DERIVATIVES **$ArC(Li){=}CR_1R_2$**

Knorr, R. *et al., Tetrahedron Lett.*, 1977, 3969
In the preparation and use of a series of 5 variously substituted 1-aryl-1-vinyllithium derivatives (Ar = phenyl, dimethylphenyl or isopropylphenyl; R_1 = H, Me or 4-tolyl; R_2 = D, Me or 4-tolyl), all operations had to be under purified nitrogen to prevent explosion.
See related ALKYLMETALS

ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

1. Bretherick, L. in *Chemical Process Hazards with Special Reference to Plant Design-V*, 1—15, Kneale, M. (Ed.), Symp. Ser. No. 39a, London, IChE, 1975
2. Grewer, T., *Runaway Reactions*, 1981, Paper 2/E, 1—18
3. Coates, C. F. *et al., Runaway Reactions*, 1981, Paper 4/Y, 1—18; *Chem. & Ind.*, 1981, 84—88
4. Dollimore, D., *Chem. & Ind.*, 1981, 196
5. Kohlbrand, H. T., *Chem. Eng. Progr.*, 1985, **81**(4), 52·
6. Gustin, J. L., *J. Loss Prev.*, 1993, **6**(5), 275
7. Fukayama, I. *et al., Bull. Fac. Eng. Yokohama Natl. Univ.*, 1984, **33**, 59—68
8. Yoshida, T. *et al., Kogyo Kayaku*, 1987, **48**(5), 311—316 (*Chem. Abs.*, 1988, **108**, 58900)
9. Cronin, J. L. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 113—132, Oxford, Pergamon, 1987
10. Itoh, M., *Kogyo Kayaku*, 1988, **49**(1), 47—52 (*Chem. Abs.*, 1988, **109**, 8938)
11. Kaneko, Y. *et al., Kogyo Kagaku*, 1988, **49**, 168—175 (*Chem. Abs.*, 1988, **109**, 233687)
12. RSST Brochure, Fauske Associates, 1988, Burr Ridge (IL)
13. Leggett, D. J., *Thermochim Acta*, 2001, 367/68, 351

Literature sources of information available to early 1974 and related to assessment of reactive chemical hazards were listed, grouped and discussed in relation to the type of information made available and their application to various situations. Eighty references are given, and those considered suitable for the nucleus of a small safety library are indicated. Toxic hazards are not covered [1]. Relatively simple procedures (oven or Dewar flask tests at normal or elevated pressures) can give a good indication of the potential for exothermic decomposition and runaway reaction hazards, as shown by initial exotherm temperatures, quasi-adiabatic self-heating curves and induction times obtained by these methods [2]. A reliable programme to screen existing, new or modified processes or products for thermal instability has been devised, suitable for a small batch manufacturing installation. This involves a progressive series of tests using simple equipment, for which constructional details are given [3]. Certain practical aspects of the programme were criticised [4]. The Dow reactive chemicals testing programme used to assess the potential hazards in pilot plant operations is outlined [5]. A Rhone Poulenc procedure based on literature, calculation and calorimetry is described in detail [6].

A simple evaluation method has been developed to assess the hazards of substances, including those regarded as non-explosive, involving thermal sensitivity, mechanical energy sensitivity and detonation sensitivity tests [7]. A method has been developed for predicting the fire and explosion hazards of new chemicals based upon two measurements of thermal properties. These are the heat of decomposition by sealed cell DSC, and the extrapolated decomposition onset temperature by ASTM E-537. These results are used in conjunction with scatter diagrams derived from the results of various standard explosive testing methods and known explosive substances [8]. A simple Insulated Exotherm Test for assessing thermal decomposition hazards, and a Power Compensated Dewar Calorimeter for measuring heat release in liquid systems are key elements in a strategy to assess thermal hazards in batch chemical manufacturing operations [9]. The method in [8] above has been further developed by running comparative tests on different DSC and DTA instruments and analysing the results statistically. Some specific practical problems are identified [10]. A procedure for such assessment, with a view to large scale processing in the real world of uncertain data and regulatory demands, is summarised. Various calorimetric techniques are combined, and an example of accident analysis given [13]. A method to determine the detonation/deflagration propagation capabilities of moderately unstable (borderline) chemicals using a propagation tube test has been developed, and the results compared with those from standard explosive tests and DSC methods. Added aluminium oxide was used as inert dephlegmator, and its mixtures with ammonium nitrate (95—100%), 1,3-dinitrobenzene (60—70%), 2,4-dinitrotoluene (70—80%), and dinitrosopentamethylene tetramine (70—80%) would propagate detonation, and dibenzoyl peroxide with 10-15% water content would propagate deflagration [11]. A new and relatively simple test instrument, the Reactive System Screening Tool (RSST) for the rapid assessment of self heating and runaway reaction potential has been described. The sample is contained in an open 10 ml spherical glass cell fitted with internal heater, thermocouple, magnetic stirrer and reagent port. The cell fits into a lagging jacket within a sealable 0.5 l stainless outer pressure vessel of 34 bar working pressure which is fitted with pressure sensor, relief line and reagent syringe. The control unit, which may be interfaced with a personal computer, will set heating rates between 0.1°C/min. and very high rates, to simulate exposure of the sample to fire conditions. For volatile materials, back pressure (e.g. 20 bar) may be applied to suppress evaporation effects. The equipment may be used to acquire data applicable to thermal evaluation or to DIERS vent-sizing purposes, and the test results are comparable with those from other thermal assessment tests. Results for methanol—acetic anhydride, and for styrene—benzoyl peroxide systems are presented graphically [12].

There are now (2005) many commercial organisations offering hazard evaluation and safety assessment, partly as a result of this, papers on the topic appear weekly. Most repeat established exhortations.

Late decades have seen great and rapid advances in many of the specialised areas of this broad topic, and some of these are covered in the topic headings:

*ACCELERATING RATE CALORIMETRY
CALORIMETRY
CHEMICAL STABILITY/REACTIVITY ASSESSMENT
COMPUTATION OF REACTIVE CHEMICAL HAZARDS
EXOTHERMIC DECOMPOSITION REACTIONS
HEAT FLOW CALORIMETRY
HIGH RATE DECOMPOSITION
MAXIMUM REACTION HEAT
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION
REACTION SAFETY CALORIMETRY
RUNAWAY REACTIONS
SCALE OF WORK
THERMAL EXPLOSIONS
THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS
THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION
See PRESSURE RELIEF (reference 6)

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

1. Bretherick, L., *Hazards in the Chemical Laboratory*, 34, London, Royal Society of Chemistry, 3rd edn., 1981
2. Everett, K., *Chem. Brit.*, 1983, **19**, 108
3. Melucci, R. C., *J. Chem. Educ.*, 1983, **60**(3), 238
4. Everson, R. J., *Chem. Eng. News*, 1987, **65**(25), 2
5. Anon., *Fire Prev.*, 1988, (213), 44—45

Care is necessary with acetylene-fed AAS burners to prevent air being drawn up the liquid drainage line, when explosion is likely [1]. While setting up an AAS instrument for use with nitrous oxide—acetylene, an explosion occured shortly after switching from compressed air to the oxide, when the flame became unstable. This was attributed to the outdoor location of the nitrous oxide cylinder (at 5°C) and the expansion cooling (4°C) occurring in the reducing valve, combining to reduce the oxide flow to the point of flame instability and flashback [2]. It was proposed that in student laboratories, air—acetylene flame sources should be replaced by air—natural gas flames to improve safety aspects with very little fall-off in detection limits in instrumental AA metal determinations [3]. Three further incidents involving explosions in AAS installations are reported. One involved accidental contamination of the acetylene inlet line by liquid acetone from an overfilled acetylene cylinder. The other

explosions involved leakage of acetylene gas inside the instrument cases and ignition by the electrical controls. Fitting of acetylene sensors inside such instruments to prevent further incidents is suggested [4]. Acetylene gas leaking from a supply tube was ignited by the source flame and a minor explosion occurred, and appears to have damaged both gas supply lines, which led to a second major explosion and fire. This involved some 6 m^3 of acetylene and 18 m^3 of nitrous oxide, and caused severe structural damage [5].
See Perchloric acid: Acetylene, Nitrous oxide
See SILVER ACETYLIDE (reference 3)

AUTOIGNITION INCIDENTS

Some incidents which have involved autoignition under unexpected circumstances may be found under the entries:
See MILK POWDER
 Calcium stearate, 3890
 Methaneboronic anhydride—pyridine complex, 0426
 Phenylchlorodiazirine, 2669
 Thiophosphoryl chloride difluoride, 3974

AUTOIGNITION TEMPERATURE

1. Hilado, C. J. *et al., Chem. Eng.*, 1972, **79**(19), 75—80
2. *Fire Hazard Properties of Flammable Liquids, Gases, Solids*, No. 325M, Boston, NFPA, 1969
3. Shimy, A. A., *Fire Technol.*, 1970, **6**, 135—139
4. Madej, T. *et al., Chem. Abs.*, 1978, **89**, 203300
5. Hilado, C. J. *et al., Fire Technol.*, 1972, **8**, 218—227
6. Bodurtha, 1980, 29
7. Hedden, K. *et al., Chem. Ing. Tech.*, 1979, **51**, 806—809
8. Lewis, D. J., *Proc. 7th Symp. Chem. Process Hazards*, Symp. Ser. No. 58, 257—271, Rugby, IChE, 1980
9. Affens, W. A. *et al., Loss Prev.*, 1980, **13**, 83—88
10. Coffee, R. D., *Loss Prev.*, 1980, **13**, 74—82
11. D'Onofrio, E. J., *Loss Prev.*, 1980, **13**, 84—97
12. Sheldon, M., *Fire Prev.*, 1983, (161), 31—37
13. Suzuki, T., *Fire Mater.* 1994, **18**(2), 81
14. Ashmore, F. S. *et al., Loss Prev. Bull.*, 1987, (075), 1—10
15. Snee, T. J., *Loss Prev. Bull.*, 1988, (091),25—38
16. Bond, 1991, 21

Autoignition temperature (AIT) is the temperature at which a material in contact with air undergoes oxidation at a sufficiently high rate to initiate combustion without an external ignition source. Although only those compounds with unusually low AIT's (225°C or below) have been included in this Handbook, there is a compilation of data for over 300 organic compounds, which also includes the theoretical background and discussion of the effect of variations in test methods upon AIT values obtained [1]. Further AIT data are given in the tabulated publication [2]. Semi-empirical formulae, based only on molecular structure, have been developed which allow AITs to be calculated for hydrocarbons and alcohols, usually with a reasonable degree of accuracy. Flammability limits, flash points, boiling points and flame temperatures may also be calculated for these classes [3]. An equation has been developed which relates the AIT of vapours and gases to the reciprocal of their induction times to self ignition [4]. The effect of iron oxide in lowering the AITs of 21 organic compounds to around 290°C [5] may mean in practical terms that this is the maximum AIT for organic compounds in contact with rusted steel or iron [6].

An improved method for determining the AIT of solids has been described, and the effect of catalytically active inorganics on the reactivity and ignition temperature of solid fuels has been studied. Sodium carbonate markedly lowers the ignition temperatures of coal and coke [7]. The volume of the vessel (traditionally a 200 ml flask) used to determine AIT has a significant effect on the results. For volumes of $1 m^3$ or greater, AIT values are appreciably lower than those measured in the standard equipment, and due allowance should be made for this [8]. The importance of the cool flame in the 2-stage autoignition process has been reviewed [9], and the transition of the cool flame via an intermediate blue flame to the hot ignition stage is discussed in detail [10]. The relationships of the 2 stages were studied for ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol and bis(2-methoxyethyl) phthalate. The latter was observed to give a transition from a cool flame to a hot flame 122°C below its minimum AIT [11]. The topic, including theoretical background, variations in testing methods and application of results, has been surveyed and summarised [12]. A procedure for calculating autoignition temperatures of organics from molecular properties. Good agreement is claimed for most of the 250 compounds examined [13].

In a further survey of AITs and their practical application, the four main factors affecting the AIT are given as: the temperature of surfaces in contact with the mixture; the contact time between these; whether the surface is active or inert; contaminants which enhance or inhibit combustion [14]. AITs are pressure sensitive, generally decreasing with increased air pressure, as also with oxygen enrichment [16]. The values determined for the various fire-related properties of combustibles (flash point, flammability limits, minimum ignition energy, and autoignition temperature) are all dependent on the particular methods used for determination, and this is especially true of the latter values, where the factors affecting the result are not well understood. The relationship between vessel size and the AITs determined therein has been studied experimentally, together with the kinetics of the slow oxidation processes which lead to ignition. Practical methods to reduce the risk of autoignition, specifically in resin manufacture are discussed, but similar considerations are likely to apply to any process involving hot fuel—air mixtures [15].

AUTOXIDATION

1. Davies, 1961, 11
2. Ingold, K. U., *Chem. Rev.*, 1961, **61**, 563
3. Kirk-Othmer, 1978, Vol. 3, 128—133

Autoxidation (interaction of a substance with molecular oxygen at below 120°C without flame [1]) has often been involved in the generation of hazardous materials from reactive compounds exposed to air. Methods of inhibiting autoxidation of organic compounds in the liquid phase has been reviewed [2,3].

See PEROXIDISABLE COMPOUNDS, α-PHENYLAZO HYDROPEROXIDES

Oxygen: Cyclohexane-1,2-dione bis(phenylhydrazone), 4825

α-Phenylazobenzyl hydroperoxide, 3603

AZIDE COMPLEXES OF COBALT(III)

1. Druding, L. F. *et al., J. Coord. Chem.*, 1973, **3**, 105
2. Druding, L. F. *et al., Anal. Chem.*, 1975, **47**(1), 176—177
3. Siebert, H. *et al., Z. Anorg. Chem.*, 1982, **489**, 77—84

A series of 12 complexes of Co(III) with both ionic and covalent azide groups was prepared and most were easily detonable as dry salts, especially at elevated temperatures [1]. Polarography is an accurate and safe method of analysis for azides [2]. Hexaammine-cobalt, -chromium and -rhodium hexaazidocobaltates are explosive, particularly in the dry state [3].

See also AMMINEMETAL AZIDES

See related METAL AZIDES

AZIDES —N_3

Many compounds of both organic and inorganic derivation, which contain the azide function, are unstable or explosive under appropriate conditions of initiation, by no means all have been given entries. The large number of compounds having entries has been subdivided for convenience on the basis of structure.

ACYL AZIDES
AMMINECOBALT(III) AZIDES
AZIDE COMPLEXES OF COBALT(III)
2-AZIDOCARBONYL COMPOUNDS
HYDRAZINIUM AZIDES
METAL AZIDES
NON-METAL AZIDES
ORGANIC AZIDES

2-AZIDOCARBONYL COMPOUNDS CO—C—N_3

1. Boyer, J. H. *et al., Chem. Rev.*, 1954, **54**, 33
2. Weyler, J. *et al., J. Org. Chem.*, 1973, **38**, 3865

Certain 2-azidocarbonyl compounds and congeners have long been known as unstable substances [1]. Some members of a group of 2,5-dialkyl-3,6-diazido-1,4-benzoquinones decompose violently on melting [2]. Individually indexed compounds are:

Azidoacetaldehyde, 0768

Azidoacetic acid, 0770

Azidoacetone, 1186

Azidoacetone oxime, 1211

2,5-Diazido-3,6-dichlorobenzoquinone, 2048
Ethyl 2,3-diazidopropionate, 1897
Ethyl 2-azido-2-propenoate, 1884
* Ethyl α-azido-*N*-cyanophenylacetimidate, 3391
Tetraazido-1,4-benzoquinone, 2629
See 2-AZIDO-2-FLUOROCARBOXYLATES

2-AZIDO-2-FLUOROCARBOXYLATES $N_3CFRCOOR'$

Preparative hazard

Takeuchi, Y. *et al., J. Fluorine Chem.*, 1994, **68**(2), 149

The activating effect of the azide makes the fluorine labile, so that there is a risk of excess azide incorporation when attempting preparation by nucleophilic substitution of bromofluorocarboxylates, giving more explosive products than anticipated.

See 2-AZIDOCARBONYL COMPOUNDS, ORGANIC AZIDES

AZIRIDINES

Several derivatives of the highly reactive aziridine (ethylenimine) show explosive instability. Individually indexed compounds are:

† Aziridine, 0859
1,1′-Biaziridinyl, 1588
Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate, 3847
1-Bromoaziridine, 0779
1-Chloroaziridine, 0782
See other STRAINED-RING COMPOUNDS

AZOCARBABORANES

Aono, K. *et al., J. Chem. Soc., Dalton Trans.*, 1981, 1190—1195

In the preparation of 1,1′-azo-2-R-1,2-dicarbadodecaborane(14) by oxidation of the aminocarbaborane anions in liquid ammonia, toluene or other inert solvent must be added before evaporation of ammonia to prevent explosions. Individually indexed compounds are:

1,1′-Azo-[2-methyl-1,2-dicarbadodecaborane(14)], 2620
1,1-′Azo-1,2-dicarbadecaborane(14), 1790
1,1′Azo-2-phenyl-1,2-dicarbadodecaborane(14), 3715

AZO COMPOUNDS C—N=N—C

Vasin, A. Ya. *et al., Chem. Abs.*, 1983, **99**, 39872

The lower concentration limits for ignition of air suspensions of 9 azo dyes have been studied. Individually indexed members of the group of unstable azo compounds are:

4-Aminophenylazobenzene, 3481
3,3′-Azo-(1-nitro-1,2,4-triazole), 1397
2,2′-Azo-3,5-dinitropyridine, 3232
Azobenzene (Diphenyldiazene), 3477
2,2′-Azobis(2,4-dimethylvaleronitrile), 3661
2,2′-Azobis(2-amidiniopropane) chloride, 3083

2,2′-Azobis(2-amidiniopropane) peroxodisulfate, 3085
Azoformaldoxime, 0811
Azoformamide, 0812
Azoisobutyronitrile, 3006
2,2′-Azoisovaleronitrile, 3339
Azomethane, 0906
Azo-*N*-chloroformamidine, 0788
Azo-*N*-methylformamide, 1596
Azo-*N*-nitroformamidine, 0821
* 2-Azoxyanisole, 3646
* 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3150
* α-(4-Bromophenylazo)benzyl hydroperoxide, 3600
* α-(4-Bromophenylazo)phenylethyl α-hydroperoxide, 3641
1-(4-Chloro-2-nitrobenzeneazo)-2-hydroxynaphthalene, 3690
5-(Diazomethylazo)tetrazole, 0715
Dicyanodiazene, 1001
Diethyl azoformate, 2419
Dimethyl azoformate, 1504
3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one, 3303
5-(4-Dimethylaminobenzeneazo)tetrazole, 3156
1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3695
* 2,2-Diphenyl-1,3,4-thiadiazoline, 3640
* Diphenyldistibene, 3494
Disodium 5-tetrazolazocarboxylate, 1008
* Disodium dicyanodiazenide, 1002
* Isopropyldiazene, 1270
Methyl 3-methoxycarbonylazocrotonate, 2826
* Methyldiazene, 0473
* α-Phenylazo-4-bromobenzyl hydroperoxide, 3601
* α-Phenylazo-4-fluorobenzyl hydroperoxide, 3602
* α-Phenylazobenzyl hydroperoxide, 3603
Potassium 4-nitrobenzeneazosulfonate, 2168
* Potassium azodisulfonate, 4658
Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide, 3599
Sodium 5(5′-hydroxytetrazol-3′-ylazo)tetrazolide, 0678

N-AZOLIUM NITROIMIDATES $N^+—N^-—NO_2$

1. Katritzsky, A. R. *et al., J. Chem. Soc., Perkin Trans 1*, 1973, 2624—2626
2. University of Southern California, *Chem. Abs.* 1994, **120**, 80853

Some of the internal salts derived from *N*-heterocycles are dangerously explosive solids, sensitive to modest heating and to impact, also liable to violent spontaneous decomposition, even in solution. A related *N*-nitroimide (hetero-N—NH—NO_2) was also explosive. It is possible the benzotriazolium imidates were also, in fact, the tautomeric nitroaminobenzotriazoles. None of their potassium salts exploded [1]. Related chemistry has been examined with a view to new explosives, in particular

1,4-bis(nitroamino)-1,4-diazabicyclo[2.2.2]octane, said to be surprisingly stable[2]. The individually indexed unstable compounds are:
Benzimidazolium 1-nitroimidate, 2700
Benzotriazolium 1-nitroimidate, 2274
Benzotriazolium 2-nitroimidate, 2275
4-Nitroamino-1,2,4-triazole, 0773
See other HIGH-NITROGEN COMPOUNDS, N—NITRO COMPOUNDS

BATS

1. Anon., *Chemical Engineer*, 1993, 546/7, 33
2. Various, *Chem. Eng. News*, 1993, **71**(38), 64; **71**(41), 60

An explosion demolishing an empty building was dubiously attributed to ignition of methane evolved from bat droppings [1]. There was much argument as to the probability of this [2], the eventual conclusion being that sewer gas from a septic tank was responsible.
See also INDIGESTION

BATTERIES

1. Anon., *Loss Prev. Bull.*, 1992, (108), 28
2. Anon., *Universities' Safety Assoc. Safety News*, 1979, (12), 20—21
3. *See entries under* Lithium
4. *Battery Hazards and Accident Prevention*, Levy, S. C. & Bro, P., New York, Plenum Press, 1994
5. Banner, J. A. *et al., J. Power Sources*, 1997, **65**, 271
6. Wang, Q. *et al., Chem. Abs.*, 2005, **142**, 264309c

Electrical batteries have associated explosion dangers. These are best known as gas evolution and explosion consequent upon over charging during recharge [1] or connection with reversed polarity: Of 3 HP7 zinc-carbon batteries inserted into a calculator, one was inserted wrongly with reversed polarity. After 2 days, when it was taken out to rectify the error, the battery 'exploded', the carbon rod being ejected with considerable force [2]. With more powerful cells, the risk is increasingly the chemical energy contained in the cell [3,6]. Short circuits can also serve as ignition sources in flammable surroundings. A book covering all aspects of safety with many types of cell has been published. It gives accounts of many incidents [4]. An anecdotal paper covers the safety issues, particularly for lithium cells [5].
See also Silver: Electrolytes, Zinc
See ELECTROLYSIS
See also STEEL

BENZENE ISOMERS C_6H_6

Editor's comments.
There are some 40 structural isomers which seem stable enough to be isolated. Six enjoy individual entries in Part I, others are less well described. All will be of higher energy

than benzene, itself endothermic, all should be suspected capable of causing explosion. To a lesser degree, non-aromatic isomers of substituted benzenes will also be suspect.
See ENDOTHERMIC COMPOUNDS

BENZYL COMPOUNDS $PhCH_2$—

Several benzyl derivatives exhibit potentially hazardous properties arising from the activation by the adjacent phenyl group, either of the substituent or of a hydrogen atom. Halides, in particular, are prone to autocatalytic Friedel Crafts polymerisation if the aromatic nucleus is not deactivated by electron withdrawing substituents. Individually indexed compounds are:

Barium *N*-perchlorylbenzylamide, 3642
Benzyl alcohol, 2802
Benzyl azide, 2775
Benzyl bromide, 2731
Benzyl chloride, 2734
Benzyl fluoride, 2742
Benzyl nitrate, 2761
1-Benzyl-3-(4-tolyl)triazene, 3650
Benzylamine, 2808
Benzyldimethylamine, 3162
Benzyloxyacetylene, 3127
* Benzylsilane, 2828
* Benzylsodium, 2783
1,2-Bis(chloromethyl)benzene, 2941
4-Bromomethylbenzoic acid, 2921
5-Chloro-2-nitrobenzyl alcohol, 2714
4-Chloro-2-nitrobenzyl alcohol, 2712
6-Chloro-2-nitrobenzyl bromide, 2667
4-Chloro-2-nitrobenzyl chloride, 2675
4-Chloro-3-nitrobenzyl alcohol, 2713
2-Chloro-4-nitrobenzyl chloride, 2674
2-Chloro-5-nitrobenzyl alcohol, 2711
Dibenzyl ether, 3648
Dibenzyl phosphite, 3651
Dibenzyl phosphorochloridate, 3643
Mercury(II) *N*-perchlorylbenzylamide, 3644
4-Methoxybenzyl chloride, 2957
3-Methoxybenzylamine, 2992
4-Methylbenzyl chloride, 2954
2-Nitrobenzyl alcohol, 2765
3-Nitrobenzyl alcohol, 2766
4-Nitrobenzyl alcohol, 2767
2-Nitrobenzyl chloride, 2710
Phenylacetonitrile, 2929
2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile), 3616

Tribenzylarsine, 3816

See also 2-HALOMETHYL-FURANS OR THIOPHENES, NITROBENZYL COMPOUNDS, α-PHENYLAZO HYDROPEROXIDES

BIS(ARENEDIAZO) OXIDES **$(ArN{=}N)_2O$**

1. Bamberger, E., *Ber.*, 1896, **29**, 451
2. Kaufmann, T. *et al., Ann.*, 1960, **634**, 77

Action of alkalies on diazonium solutions, or of acids on alkali diazoates to give a final pH of 5—6, causes these compounds ('diazoanhydrides') to separate as oils or solids. Many of these are violently explosive (some exceeding nitrogen trichloride in effect), sensitive to friction and heat or contact with aromatic hydrocarbons [1,2]. Individually indexed compounds are:

Bis(2,4,5-trichlorobenzenediazo) oxide, 3425

Bis(4-chlorobenzenediazo) oxide, 3450

Bis(benzeneazo) oxide, 3484

Bis(toluenediazo) oxide, 3647

See related BIS(ARENEDIAZO) SULFIDES below

BIS(ARENEDIAZO) SULFIDES **$(ArN{=}N)_2S$**

Some of the products of interaction of diazonium salts with sulfides may have this structure. Relevant entries are:

Bis(4-nitrobenzenediazo) sulfide, 3461

Bis(benzenediazo) sulfide, 3485

See DIAZONIUM SULFIDES AND DERIVATIVES

BIS(DIFLUOROAMINO)ALKYL NITRATES **$F_2NCRCH(NF_2)ONO_2$**

Reed, S. F., *J. Org. Chem.*, 1972, **37**, 3329—3330

Prepared from tetrafluorohydrazine and alkenyl nitrates, these compounds are dangerously explosive. Purification is difficult, as they are sensitive to heat and shock. Preparation by nitration of the alcohol is a more practical route.

See other DIFLUOROAMINO COMPOUNDS

BIS(FLUOROOXY)PERHALOALKANES **$F_3CCCl(OF)_2$ etc.**

Hazardous preparation and products

Sekiya, A. *et al., Inorg. Chem.*, 1980, **19**, 1328—1330

The compounds are all strong oxidants and explosive, requiring very careful handling. Individually indexed compounds are:

2,2-Bis(fluorooxy)hexafluoropropane, 1059

1,1-Bis(fluorooxy)hexafluoropropane, 1058

1,1-Bis(fluorooxy)tetrafluoroethane, 0637

2-Chloro-1,1-bis(fluorooxy)trifluoroethane, 0592

1,1,4,4-Tetrakis(fluoroxy)hexafluorobutane, 1370

See Fluorine: Fluorocarboxylic acids, etc.
See related HYPOHALITES

BIS(SULFUR)DIIMIDES **$Z(N{=}S{=}NR)_2$**

Appel, R. *et al., Chem. Ber.*, 1976, **109**, 2444

During the preparation of a series of the bis(diimides), ($Z = (CH_2)_{2\text{ or }3}$; R = Me, Et), work-up operations must be at below 100°C to avoid violent decomposition.

See other N—S COMPOUNDS

BITUMEN

1. Agaev, A. S. *et al., Chem. Abs.*, 1975, **82**, 88310
2. Hoban, T. W. S. *et al., J. Loss Prevention*, 1994, **7**(3), 217

Factors leading to ignition or explosion during preparation of high-melting bitumens by air-blowing petroleum residues were identified as control of vapour temperature (often above AIT), presence of lower hydrocarbon vapours, and lack of control of free oxygen content. Measures for controlling these are discussed [1]. Bitumen storage tank fires are instanced, and the causes discussed [2].

See Oxygen: Hydrocarbons

BLEACHING POWDER **$Ca(OCl)_2,4H_2O.CaCl_2,Ca(OH)_2,H_2O$**

1. Mellor, 1956, Vol. 2, Suppl. 1, 564—567
2. *Accid. Bull. No. 30*, Washington, Amer. Railroad Assoc. Bur. Explos., 1921
3. Gill, A. H., *Ind. Eng. Chem.*, 1924, **16**, 577
4. ‘Leaflet No. 6’, London, Inst. Chem., 1941

Bleaching powder is effectively a mixture of calcium hypochlorite, calcium hydroxide and a non-hygroscopic form of calcium chloride [1] and may therefore be regarded as a less active form (39% available chlorine) of oxidant than undiluted calcium hypochlorite (49% chlorine). There is a long history of explosions, many apparently spontaneous, involving bleaching powder. On storage or heating, several modes of decomposition are possible, one involving formation of chlorate which may increase the hazard potential. Of the 3 possible routes for thermal decomposition, that involving liberation of oxygen predominates as the water content decreases, and at 150°C the decomposition becomes explosive [1]. Material which has been stored for a long time is liable to explode on exposure to sunlight, or on overheating of tightly packed material in closed containers [2]. The spontaneous explosion of material packed in drums was attributed to catalytic liberation of oxygen by iron and manganese oxides present in the lime used for manufacture [3]. Traces of metallic cobalt, iron, magnesium or nickel may also catalyse explosive decomposition [1]. When the lever-lid of a 6-month-old tin of bleaching powder was being removed, it flew off with explosive violence, possibly owing to rust-catalysed slow liberation of oxygen [4].

Bis(2-chloroethyl) sulfide

Mellor, 1956, Vol. 2, Suppl. 1, 567

Interaction is very exothermic and ignition may occur, particularly in presence of water.

Wood

Anon., *ABCM Quart. Safety Summ.*, 1933, **4**, 15

A mixture of sawdust and bleaching powder ignites when moistened.

See other METAL HYPOCHLORITES, OXIDANTS

BLEVE

1. Prugh, R. W., *Chem. Eng. Progress*, 1991 (Feb.), 66
2. Venart, J. E. S. *et al., Process Safety Progr..*, 1993, **12**(2), 67
3. Birk, A. M. *et al., J. Loss Prev.*, 1994, **7**(6), 474
4. Birk, A. M. *et al., Chem. Abs* ., 1998, **129**, 323897d

A Boiling Liquid Expanding Vapour Explosion, or BLEVE, is an industrial event related to the laboratory 'bump' occasioned when the inadequately mixed bottom of a vessel of liquid becomes superheated, then explosively boils. In the industrial version, rupture of a pressurised container is usually involved. Although strictly speaking a non-reactive physical hazard, chemical fires and explosions, with fatalities, often follow. Means of estimating risk and prevention, with a list of incidents are given [1]. A more ferocious version, the Boiling Liquid Compressed Bubble Explosion, or BLCBE, involving multiple site initiation during the explosive stage, is described [2]. A study of Bleves in propane tanks is combined with a procedure for predicting whether a tank will BLEVE or merely produce a jet leak on overheating [3]. The relationship between BLEVE conditions and subsequent fireballs has been studied [4]

See also VAPOUR CLOUD EXPLOSIONS

BLOWING AGENTS

1. Morisaki, S. *et al., J. Haz. Mat.*, 1981, **5**, 49—63
2. Bond, J., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 37—44, Oxford, Pergamon, 1987

Six blowing agents (* in the list below), which generate gas (mainly N_2) by thermal decomposition and are used to create plastic foams, were examined by DSC at up to 50 bar pressure. The very significant increase in heat release under pressure (especially air pressure) suggests that sealed containers of the materials may explode violently if subjected to heating [1]. Decomposition of a hydrazide blowing agent in a large feed hopper was probably initiated by friction from the mechanical feed-screw in the base. The exothermic decomposition activated the explosion suppression system which added to the volume of gas produced and caused rupture of the hopper [2].

Individually indexed compounds are:

2,2′-Azobis(2,4-dimethylvaleronitrile), 3661
Azoformamide*, 0812
Azoisobutyronitrile*, 3006
2,2′-Azoisovaleronitrile*, 3339
Azo-*N*-methylformamide, 1596
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane*, 1948

4,4′-Oxybis(benzenesulfonylhydrazide)*, 3519
4-Toluenesulfonylhydrazide*, 2823
See also RADICAL INITIATORS

BORANES (BORON HYDRIDES)

Wright,S. W. *et al., Chem. Eng. News*, 1992, **70**(35), 4
Many boranes and their complexes are air sensitive and pyrophoric. Boranes and their complexes apparently disproportionate to higher boranes and hydrogen on storage, pressurising their containers.

Only unsubstituted boranes and their complexes are grouped here, alkylated or halogenated derivatives are have their own entries
Individually indexed compounds are:

∗ Ammonium decahydrodecaborate(2—), 0199
∗ 1,1′-Azo-[2-methyl-1,2-dicarbadecaborane(14)], 2620
∗ Bis(borane)—hydrazine, 0143
∗ Bis(dimethylaminoborane)aluminium tetrahydroborate, 1789
∗ *N,N*-Bis(trimethylsilyl)aminoborane, 2608
Borane, 0135
∗ Borane—ammonia, 0141
∗ Borane—bis(2,2-dinitropropylhydrazine), 0137
Borane—dimethylsulfide, 0136
∗ Borane—hydrazine, 0142
∗ Borane—phosphorus trifluoride, 0140
∗ Borane—pyridine, 0139
∗ Borane—tetrahydrofuran, 0138
∗ *N-tert*-Butyl-*N*-trimethylsilylaminoborane, 2873
∗ *B*-Chlorodimethylaminodiborane, 0958
∗ Cyanoborane oligomer, 0392
Decaborane(14), 0198
∗ Diammineboronium heptahydrotetraborate, 0190
∗ Diammineboronium tetrahydroborate, 0167
† Diborane(6), 0166
∗ Dimethylaminodiborane, 0963
∗ Disodium tridecahydrononaborate(2—), 0195
∗ Heptakis(dimethylamino)trialuminium triboron pentahydride, 3669
Hexaborane(10), 0191
Hexaborane(12), 0192
Pentaborane(11), 0189
† Pentaborane(9), 0188
∗ Phosphorus azide difluoride—borane, 4310
Poly[borane(1)], 0134
Tetraborane(10), 0181
∗ Tetraphosphorus hexaoxide—bis(borane), 4862

See ALKYLBORANES, ALKYLHALOBORANES, 1,3-DIAZA-2-BORACYCLOALKANES, HALOBORANES

See other NON-METAL HYDRIDES

Aluminium chloride, Sulfur dioxide

Bonnetot, B. *et al., Inorg. Chim. Acta*, 1989, **156**(2), 183

Intimate mixtures or complexes of the above and salts of decahydrodecaborate(2—) left after evaporation of excess liquid sulfur dioxide exploded on grinding. The same could presumably happen with derivatives of other boranes.

Carbon tetrachloride

1. Hermanek, S., *Chem. Abs.*, 1976, **84**, 38384
2. *491M*, 1975, 92

Carbon tetrachloride is not recommended as an eluting solvent in the chromatographic separation of boranes, carbaboranes or their derivatives because of the danger of explosion [1]. Use of a carbon tetrachloride extinguisher on a diborane fire caused a violent explosion [2].

BORON COMPOUNDS

This class contains the groups:

ALKYLBORANES
ALKYLHALOBORANES
AZOCARBABORANES
BORANES
CARBABORANES
DIAZONIUM TETRAHALOBORATES
HALOBORANES

tert-BUTYL ESTERS $Me_3COCO.R$

Hodgson, P. K. G. *et al., J. Chem. Soc., Perkin Trans. 2*, 1978, 854

Preparation of *tert*-butyl esters from the acid and 2-methylpropene under pressure in glass vessels led to explosions. A safe procedure in a steel cylinder is described.

tert-BUTYL PEROXOPHOSPHATE DERIVATIVES $Me_3COOP(O)(OR)_2$

Rieche, A. *et al., Chem. Ber.*, 1962, **95**, 381—388

Although dialkyl *tert*-butylperoxophosphate derivatives are relatively stable, the diaryl esters and bis(*tert*-butylperoxo) esters decompose violently on attempted isolation. Individually indexed compounds are:

O—O-tert-Butyl di(4-tolyl) monoperoxophosphate, 3757
O—O-tert-Butyl diphenyl monoperoxophosphate, 3706
tert-Butyl peroxophosphoryl dichloride, 1639
Di(*O—O-tert*-butyl) ethyl diperoxophosphate, 3368
See related PEROXYESTERS, PHOSPHORUS ESTERS

CALORIMETRY

Individual entries:

ACCELERATING RATE CALORIMETRY (ARC)
ADIABATIC CALORIMETRY
ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
CHEMICAL STABILITY/REACTIVITY ASSESSMENT
DIFFERENTIAL SCANNING CALORIMETRY (DSC)
DIFFERENTIAL THERMAL ANALYSIS (DTA)
HEAT FLOW CALORIMETRY
OXYGEN BOMB CALORIMETRY
REACTION SAFETY CALORIMETRY
THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

CAN OF BEANS

Foote, C. S., private comm., 1965

An unopened can of beans, placed in a laboratory oven originally at 110°C but later reset to 150°C, exploded causing extensive damage. Comments were judged to be superfluous.

See Diprotium monoxide

CARBABORANES **(Cyclic boranes with hetero C atoms)**

Carbon tetrachloride

See BORANES: Carbon tetrachloride

CARBONACEOUS DUSTS

Explosion and Ignition Hazards, Rept. 6597, Washington, US Bur. Mines, 1965

Hazards of 241 industrial dusts which may explode or burn because of their carbon content are defined, covering particle size and chemical composition in 10 categories.

Carbon, (reference 6), 0297

See also DUST EXPLOSION INCIDENTS, PETROLEUM COKE

CARBON NITRIDES

There seems a considerable interest in preparing C_3N_4, or more exactly materials approximating to that. They are usually made by pyrolysis of high-nitrogen heterocyclic materials, with azide substituents, which might themselves justly be called carbon nitrides. They are usually explosive in large quantities. Other carbon nitrides, such as cyanogen, or diazomalononitrile, are also high energy. Given the relative weakness of the C-N bond compared to C-C, even the desired product will have a very positive enthalpy of formation.

See HIGH-NITROGEN COMPOUNDS, ORGANIC AZIDES

CARBONYLMETALS **$M(CO)_n$**

Bailar, 1973, Vol. 1, 1227

The explosive ‘carbonylalkali-metals’, previously formulated as monomeric compounds, are either dimeric acetylene derivatives of the general formula MOC≡COM, or are trimers of the latter and formulated as salts of hexahydroxybenzene. Many true carbonylmetal complexes are air-sensitive and pyrophoric, not always immediately. Individually indexed compounds are:

* Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum] —tetrakis(tetrahydrofuran)magnesium, 3907
* Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3785
* Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3827
Bis(dicarbonylcyclopentadienyliron)—bis(tetrahydrofuran)magnesium, 3829
* Caesium pentacarbonylvanadate(3—), 1805
* Carbonyl(pentasulfur pentanitrido)molybdenum, 0532
Decacarbonyldirhenium, 3380
* Dicarbonylmolybdenum diazide, 0991
* Dicarbonyltungsten diazide, 1009
* Dicarbonyl-η-trichloropropenyldinickel chloride dimer, 3227
* Dicarbonyl-π-cycloheptatrienyltungsten azide, 3117
Dodecacarbonyltetracobalt, 3414
Dodecacarbonyltriiron, 3422
Hexacarbonylchromium, 2049
Hexacarbonylmolybdenum, 2624
Hexacarbonyltungsten, 2632
Hexacarbonylvanadium, 2631
* Hexakis(pyridine)iron(II) tridecacarbonyltetraferrate(2—), 3900
* Lithium octacarbonyltrinickelate, 3102
Nonacarbonyldiiron, 3105
Octacarbonyldicobalt, 2876
† Pentacarbonyliron, 1808
* Potassium pentacarbonylvanadate(3—), 2043
* Potassium tricarbonyltris(propynyl)molybdate(3—), 3464
* Sodium pentacarbonylrhenate, 2045
* Sodium tetracarbonylferrate(2—), 1372
* Tetracarbonylmolybdenum dichloride, 1354
† Tetracarbonylnickel, 1799
* Tetrakis(pyridine)bis(tetracarbonylcobalt)magnesium, 3861
* 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate, 3179
* 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, 3180
* Tris(bis-2-methoxyethyl ether)potassium hexacarbonylniobate(1—), 3850

CATALYST HANDLING SAFETY

1. Fulton, J. W., *Chem. Eng.* (NY), 1987, **94**(12), 99—101
2. Habermehl, R., *Chem. Eng. Progr.*, 1988, **84**, 16—19
3. Reynolds, M. P. *et al., Chem. Ind.* (Dekker), 1996, **68**, 371

Safety aspects of drum storage, pellet screening, dust removal, reactor loading and unloading, and activation of process catalysts are discussed [1], and reprocessing

aspects are considered, with disposal as a last resort [2]. Hydrogenation catalysts introduce their own problems [3].
See also HYDROGENATION CATALYSTS

CATALYTIC HYDROGENATION AUTOCLAVES

Harak, J., *Stud. Surf. Sci. Catal.*, 1986 (27, Catal. Hydrog.), 578—611
Measures and equipment needed for safe control of autoclaves used for laboratory, pilot plant, or industrial scale catalytic hydrogenation are discussed, including the need for early recognition of onset of hazardous conditions.
HYDROGENATION CATALYSTS
HYDROGENATION INCIDENTS
See also CATALYTIC NITRO REDUCTION PROCESSES

CATALYTIC IMPURITY INCIDENTS

Incidents where presence of impurities, often in trace (catalytic) amounts, has significantly reduced stability or enhanced reactivity are under the entries:
Acetic anhydride, : Ethanol, Sodium hydrogen sulfate, 1529
† Acrylaldehyde, 1142
Adipic acid, 2435
Ammonium perchlorate, : Impurities, 3998
Azidoacetic acid, 0770
† Aziridine, : Acids, 0859
Benzoyl azide, 2694
Benzyl chloroformate, 2926
1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0799
Bromine trioxide, 0259
2-Butanone oxime, 1649
2-Butyne-1,4-diol, 1523
Butyraldehyde oxime, 1650
Carbon, : Unsaturated oils, 0297
Chlorine, : Carbon disulfide, 4041
† 1-Chloro-2,3-epoxypropane, : Contaminants, 1158
Cyanogen chloride, 0322
* Diethyl phosphorochloridate, 1675
† 1,1-Difluoroethylene, 0696
† Diketene, : Acids, or Bases, or Sodium acetate, 1437
N,N-Dimethylacetamide, 1651
2,4-Dinitrotoluene, 2722
4-Ethoxy-2-methyl-3-butyn-2-ol, 2840
Ethyl oxalyl chloride, 1452
Ethylene oxide, : Contaminants, 0825
Hydrogen peroxide, : Coal, 4471
Hydrogen peroxide, : Copper(II) chloride, 4471
† Isopropyl chloroformate, 1555
Maleic anhydride, : Bases, or Cations, 1400

Mercury(II) oxalate, 0978
* Methyl isocyanoacetate, 1466
Methylammonium nitrate, 0503
4-Methylbenzyl chloride, 2954
N-Methylmorpholine oxide, 1991
Nickel, : Hydrogen, Oxygen, 4814
Nitric acid, : Sulfur dioxide, 4430
Oxygen difluoride, : Hexafluoropropene, Oxygen, 4311
Oxygen (Gas), : Carbon disulfide, Mercury, Anthracene, 4825
Oxygen (Liquid), : Carbon, Iron(II) oxide, 4826
Potassium chlorate, : Manganese dioxide, 4011
† Propionyl chloride, : Diisopropyl ether, 1159
† Propylene oxide, : Sodium hydroxide, 1221
Silver azide, 0023
Silver nitride, 0038
Sodium carbonate, 0549
Sodium peroxoborate, 0155
Tetrafluoroammonium tetrafluoroborate, 0133
Triallyl phosphate, 3178
Trifluoromethanesulfonic acid, : Acyl chlorides, Aromatic hydrocarbons, 0374
Trimethyl phosphate, 1314
See DIAZONIUM TETRAHALOBORATES (reference 5), INDUCTION PERIOD INCIDENTS

CATALYTIC NITRO REDUCTION PROCESSES $RNO_2 \nRightarrow RNH_2$

1. MacNab, J. I., *Runaway Reactions*, 1981, Paper 3/S, 1—15
2. Stoessel, F., *J. Loss Prev.*, 1993, **6**(2), 79

Catalytic reduction of aromatic nitro compounds to the amines is highly exothermic ($\Delta H = -548 \pm 12$ kJ/mol) and has high potential for hazard in the event of cooling- or other process-failure. The total reaction proceeds *via* nitroso and hydroxylamino intermediates, both of which are reactive and may undergo undesired condensation or disproportionation reactions, and the thermochemistry of all these possibilities was investigated. The reduction or disproportionation of the hydroxylamino intermediate (which is of low thermal stability) is identified as the fastest and most exothermic step (despite which it can frequently be concentrated or trapped); implications for process safety are considered in detail and verified by experiment with typical compounds and intermediates [1]. A calorimetric study of the hazards inherent in hydrogenation of nitroaromatics was made, using nitrobenzene as model compound [2]. Individual incidents of this type are:
2-Chloro-5-methylphenylhydroxylamine, 2792
3,4-Dichlorophenylhydroxylamine, 2236
2-Nitroanisole, : Hydrogen, 2764
1,1,1-Tris(azidomethyl)ethane, 1931
Tris(hydroxymethyl)nitromethane, 1658
See also CALORIMETRY, CATALYTIC HYDROGENATION AUTOCLAVES

CATHODIC CORROSION PROTECTION

Bond, 1991, 43; *ibid.*, 63

Cathodic protection systems have started a number of hydrocarbon fires, either by direct current sparking to earth, or from thermite reactions causing sparks when rusty lumps of iron fall on magnesium electrodes.

See THERMITE REACTIONS

CELLULOSE $(C_6H_{10}O_5)_n$

Gray, B. F. *et al., J. Chem. Technol., Biotechnol.*, 1984, **34A**(8), 453—463

Spontaneous ignition hazards and criteria for safe storage of stockpiles of cellulosic materials were investigated on the laboratory scale, using piles of sieved bagasse pith of various sizes and shapes. Temperature profiles were measured and critical temperatures for ignition determined with high accuracy. The important part played by moisture was investigated, and the need for improvement in scaling extrapolation procedures is stressed. The results are consistent with those for wood flour, and conclusions are applicable to all cellulosic materials at high temperatures.

Energy of exothermic decomposition of finely fibrous cellulose in range 275—335°C was measured as 0.32kJ/g.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Calcium oxide

See Calcium oxide: Water (reference 2)

Oxidants

See Calcium permanganate: Cellulose
  Fluorine: Miscellaneous materials, 4304
  Magnesium perchlorate: Cellulose, etc., 4078
  N-Methylmorpholine oxide, 1991
  Nitric acid: Cellulose, 4430
  Perchloric acid: Cellulose and derivatives, 3992
  Perchloric acid: Hydrofluoric acid, Structural materials, 3992
  Potassium chlorate: Cellulose, 4011
  Potassium nitrate: Cellulose, 4645
  Sodium chlorate: Paper, etc., or : Wood, 4033
  Sodium nitrate: Fibrous material, 4716
  Sodium nitrite: Wood, 4715
  Sodium peroxide: Fibrous materials, 4797
  Zinc permanganate: Cellulose, 4705
BLEACHING POWDER: Wood
PERCHLORATES: Organic matter
See SUGARS

Water

1. Longauerova, D. *et al., Chem. Abs.* 1993, **118**, 26762
2. Kletz, T. A., *Process Safety Progress*, 1995, **14**(4), 274

A storage tank for neutral sulphite woodpulp exploded. Investigation showed bacterial contamination, producing hydrogen and hydrogen sulphide in the headspace, which subsequently suffered electrostatic ignition [1]. A similar incident with ignition from welding operations is reported; in this case not bulk wet woodpulp, but recycled water from pulping operations was the source of the hydrogen [2]. [NB, much clothing and all kitchen paper are made of cellulose, neither the above phenomena, nor a very mild exotherm on hydration, justify the statement in another work on reactive chemicals that cellulose and water are an unsafe combination – Editor]
See COTTON, WOOD PULP

CELLULOSE NITRATE

(*MCA SD-96*, 1970); *FPA H118*, 1982

1. Kirk-Othmer, 1979, Vol. 5, 129—137
2. Anon., *Accidents*, 1961, **46**, 12
3. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 13
4. *MCA Case History No. 1614*
5. Fifen, R. A., *Progr. Astronaut. Aeronaut.*, 1984, **90**, 177—237
6. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62—74
7. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
8. Roberts, T. A. *et al., J. Loss Prev.*, 1992, **5**(5), 311
9. Dosoudel, T. *et al., Chem. Abs.*, 1994, **121**, 13250

Cellulose nitrate is very easily ignited and burns very rapidly or explosively, depending on the degree of confinement, degree of nitration and state of subdivision. Unless very pure and stabilised, it deteriorates in storage and may ignite spontaneously [1]. Removal of the emulsion coating from celluloid film base gives unstable material which may ignite on prolonged storage in an enclosed space [2]. Unused but aged centrifuge tubes made of ’nitrocellulose’ plasticised with dibutyl phthalate, ignited and exploded while being steam-sterilised in an autoclave at 125°C. The violent decomposition was attributed to the age of the tubes, the high temperature and the presence of the steam, (leading to hydrolysis and formation of free nitric acid) [3]. During hacksaw cutting of a pipe containing cellulose nitrate residues, a violent explosion occurred [4]. The ignition and combustion chemistry of cellulose nitrate has been reviewed, including the decomposition and catalysis mechanisms [5]. The finely divided nitrate is also a very significant dust explosion hazard, maximum explosion pressures above 17.4 bar, with maximum rate of rise above 1.42 kbar/s have been recorded [6]. Values for the critical ignition temperature of 60 and 41°C for induction periods of 7 and 60 days, respectively, have been recorded. Autocatalytic combustion is exhibited [7]. Details of storage separation distances for cellulose nitrate sufficient to prevent thermal radiation propagating deflagration from one container to the next are given [8]. Water in nitrocellulose powders does not always have the expected stabilising effects. Detonation velocities can increase and 25% water was shown to facilitate the deflagration to detonation transition [9].

Amines MRH 4.81/tr. (for all 8 amines)

1. Anon., *ABCM Quart. Safety Summ.*, 1956, **27**, 2

2. Thurlow, G. K. *et al.*, private comm., 1973

3. Kaila, E., *Chem. Abs.*, 1958, **52**, 19121_f

Cellulose nitrate of high surface area (dry or alcohol-wet guncotton or scrap) spontaneously ignited in contact with various amines used as curing agents for epoxy resins. These included 1,2-diaminoethane, *N*-2-hydroxyethyl-1,2-diaminoethane, diethylenetriamine, triethylenetetramine, *N*-2-hydroxyethyltriethylenetetramine, tetraethylenepentamine, 2-hydroxyethylamine, 2-hydroxyethyldimethylamine, 2-hydroxypropylamine, 3-dimethylaminopropylamine, morpholine, and diethylamine. Ethylamine and dibutylamine caused charring but not ignition [1]. Similar results were found during an investigation of the compatibility of cellulose nitrate with a range of amine and amide components used in paint manufacture. Preliminary small-scale (12 g) tests in which ethyl acetate solutions of cellulose nitrate and the other components were mixed in a lagged boiling tube showed large exotherms (which boiled the solvent off) with 1,4-diazabicyclo[2.2.2]octane, 2,4,6-tris(dimethylamino)phenol, morpholine and benzyldimethylamine. Smaller exotherms were shown by dodecylamine, dodecyldimethylamine (both fat-derived, containing homologues) and a polyamide resin, Versamid 140.

Subsequent tests in which small portions of these undiluted liquid amines and dried cellulose nitrate linters were contacted (with a little added butyl acetate for the solid phenol) under various conditions, gave ignition with the first 3 amines, and exotherms to 110°C with foaming decomposition for the remaining 4. Other amine resin components showed slight or no exotherms in either test [2]. Contact of cellulose nitrate with a little butylamine caused explosive reaction [3].

Iron red pigment, Plasticiser

Penczek, P. *et al., Chem. Abs.*, 1976, **85**, 63924

During roller-blending to disperse iron red pigment (iron(III) oxide) into plasticised cellulose nitrate, the mixture became a gel after 15 passes and tended to self-ignite.

Iron(II) sulfate

Yan, Z., *Chem. Abs.*, 1983, **99**, 106948

Presence of iron(II) sulfate reduces the stability of the nitrate by a factor of 2.5.

Other reactants

Yoshida, 1980, 274

MRH values calculated for 13 materials all indicate likely catalytic decomposition effects with traces of them.

Potassium iodide

Morrow, S. I., *Anal. Calorim.*, 1977, **4**, 185—191

Low levels of potassium iodide strongly retard the thermal decomposition of thin films of cellulose nitrate.

See other PYROPHORIC MATERIALS

See related ALKYL NITRATES

CHARCOAL

Pfeil, N., *Loss Prevention and Safety Promotion in the Process Industries*, Vol II, (Mewis, J. J., Pasman, H. J. and De Rademaker, E. E. Eds.), 161, Amsterdam, Elsevier, 1995

Autoignition of fresh charcoal, but not gunpowder prepared from it, is known to have happened in the black powder industry. (Optimum charcoal for gunpowder production is well short of being fully carbonised).

See Carbon

CHEMICAL PLANT SAFETY

1. Kirk Othmer, 1996, Vol 19, 190
2. Ullmann, 1995, B7, B8, especially B8, 311
3. *Loss Prevention in the Process Industries*, Lees, F. P., Oxford, Butterworth-Heinemann, 2nd Edn. (3 Volumes), 1996
4. *The Safe Handling of Chemicals in Industry*, Carson P. A., Mumford, C. J., Harlow (Essex), Longmans 1989: (originally two volumes, later extended to four)
5. *Hazards XV, Inst. Chem. Eng. Symp. Ser.*, 2000, **147**

Much writing on this subject, from introductory essays to multivolume books covering all aspects, including the legislatory and bureaucratic, has latterly appeared. Remarkably little of it is directly relevant to the purposes of this book, which is not surprising since it is slips, trips, falls and moving transport accidents which injure and kill chemical workers, far more than do fire and explosion, though these are themselves well ahead of poisoning in the accident statistics. Public concern is otherwise focussed. Some English-language examples are given above. Several papers on building and plant layout for personnel safety against fire and explosion are published in [5], along with much on other explosive aspects of plant safety.

CHEMICAL STABILITY/REACTIVITY ASSESSMENT

Fenlon, W. J., *Proc. Intern. Sympos. Prev. Major Chem. Accid.*, Washington, 1987, A.27—A.41, New York, AIChE, 1987

In the Technical Safety Laboratory of Eastman Kodak, the role played by calorimetric methods (such as High Pressue DSC and ARC techniques) in assessing the stability of chemicals and processes, though a central one, is but part of a range of techniques used for this overall purpose. The relations between these methods is discussed and presented in the form of logic flow diagrams.

COMPUTATION OF REACTIVE CHEMICAL HAZARDS

REACTION SAFETY CALORIMETRY

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

CHEMICAL VAPOUR DEPOSITION (CVD)

Hammond, M. L., *Solid State Technol.*, 1980, **23**(12), 104—109

Hazards assodiated with the use of cleaning, etching and doping materials and procedures in semi-conductor CVD are codified, with 7 references.

See also GAS HANDLING

CHLORINATED PARAFFINS

Carbon black, Lead(IV) oxide, Manganese(IV) oxide

Chlorinated paraffins are viscous liquids or low-melting solids, depending on the chlorine content (40—80%) and the paraffin type. In general they are thermally unstable, tending to eliminate hydrogen chloride. In the absence of an inhibitor (usually a material which will react readily with traces of hydrogen chloride), they will soon turn brown or black at ambient temperature. Epoxides or glycols are often used as inhibitors at around 1% concentration, and chlorinated paraffins stabilised with propane-1,2-diol or epoxidised soya oil may be heated to 100°C with little change, though for limited periods, as the inhibitor becomes depleted with time.

See Lead(IV) oxide: Carbon black, etc.

See related HALOALKANES, HALOCARBONS

N-CHLORINATED PHOSPHORUS AMIDES $(RO)_2P(O)NCl_2$

Preparative hazard

See Chlorine: Dimethyl phosphoramidates

CHLORINATED POLY(DIMETHYLSILOXANES) $(\text{-OSi(Me)(CH}_2\text{Cl)O-})_n$

Sosa, J. M., *Thermochim. Acta*, 1975, **13**, 100—104

Chlorinated silicone oil (DC200, with 15, 30 or 40% chlorine content; structure shown has 32%) decomposed violently on heating. Thermal stability decreased with increasing chlorine content and was investigated by TGA and DSC techniques.

CHLORINATED RUBBER

Metal oxides or hydroxides

1. Anon., *Chem. Trade J.*, 1962, **151**, 672
2. Anon., *Euro. Chem. News*, 1963, (May 24th), 29
3. 'Rept. GCS 27130', London, ICI, 1963
4. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 12

Intimate mixtures of chlorinated rubber and zinc oxide or powdered zinc, with or without hydrocarbon or chlorinated solvents, react violently or explosively when heated at about 216°C. If in milling such mixtures local overheating occurs, a risk of a violent reaction exists. Such risks can be minimised by controlling milling temperatures, by cooling, or by using a mixture of maximum possible fluidity [1]. Similar reactions have been observed with antimony or lead oxides, or aluminium, barium or zinc hydroxides [2]. The full report [3] has been abstracted [4].

See related HALOALKENES

CHLORINE-CONTAINING SYSTEMS

1. Mal'tseva, A. S. *et al., Chem. Abs.*, 1975, **82**, 45981
2. Dokter, T., *Explosion hazards of methyl chloride and chlorine-containing systems*, PhD thesis, Twente University, Netherlands. 1987
3. Gustin J-L., *Ind. Chem. Libr.*, 1996 **8**(Roots of Organic Development), 431, Elsevier

Explosive limits and hazards of various binary and ternary systems containing chlorine or its compounds are reviewed and discussed [1]. The safety aspects of operating a proposed pilot plant for the continuous production of dichloromethane and chloroform from chloromethane and chlorine have been studied in an explosion hazards analysis. The study has been augmented by experimental investigation of many of the safety parameters revealed in the study for which no results were available. Such parameters include flammability limits, burning velocities and quenching diameters, detonation limits and velocities, ignition energies and autoignition temperatures in the gaseous system chloromethane—dichloromethane—chlorine—hydrogen chloride; autoignition temperatures of chloromethane and dichloromethane in chlorine. Additionally, the formation of the highly explosive nitrogen trichloride during chlorination of materials containing ammonium salts or other nitrogen source was studied [2]. A review covering auto-ignition, deflagration and detonation of chlorination reactions has appeared more recently [3].

Chlorine drying towers
See Chlorine
See Hydrogen: Oxygen, Sulfuric acid

CHLORITE SALTS ClO_2^-

1. Mellor, 1941, Vol. 2, 284; 1956, Vol. 2, Suppl. II (Halogens), 573—575
2. Pascal, 1960, Vol. 16, 263

Many of the salts which have been prepared are explosive and sensitive to heat or impact. These include chlorites of copper (violent on impact), hydrazine (monochlorite, inflames when dry), nickel (explodes at 100°C but not on impact), silver (at 105° or on impact), sodium, tetramethylammonium, mercury, thallium and lead (which shows detonator properties). Several other chlorites not isolated and unstable in solution include mono-, di- and tri-methylammonium chlorites. The metal salts are powerful oxidants [1]. Chlorites are much less stable than the corresponding chlorates, and most will explode under shock or on heating to around 100°C [2]. Individually indexed compounds are:

Barium chlorite, 0204
Calcium chlorite, 3919
Hydrazinium chlorite, 4002
Lead(II) chlorite, 4096
Lithium chlorite, 4014
Mercury(I) chlorite, 4074
Mercury(II) chlorite, 4071
Methylammonium chlorite, 0497
Nickel chlorite, 4087
Potassium chlorite, 4010
Silver chlorite, 0010
Sodium chlorite, 4032
Tetramethylammonium chlorite, 1736
Thallium(I) chlorite, 4037
See also OXOSALTS OF NITROGENOUS BASES

CHLOROFLUOROCARBONS

RSC Lab. Hazard Data Sheet No. 75, 1988

Information is given on Freons 11, 12, 13, 21, 22, 113, 114: trichlorofluoro-, dichlorodifluoro-, chlorotrifluoro-, dichlorofluoro- and chlorodifluoro-methane; 1,1,2-trichloro-1,2,2-trifluoro-, and 1,2-dichloro-tetrafluoro-ethane, respectively.
1,2-Dichlorotetrafluoroethane, 0601
Trichlorofluoromethane, 0329
See Chlorodifluoromethane
See also HALOCARBONS

N-CHLORONITROAMINES $RN(Cl)NO_2$

Grakauskas, V. *et al., J. Org. Chem.*, 1972, **37**, 334
N-Chloronitroamines and the derived *N*-chloro-*N*-nitrocarbamates are explosive compounds and decompose rapidly in storage.
See N-Fluoro-*N*-nitrobutylamine
See other N-HALOGEN COMPOUNDS, N—NITRO COMPOUNDS

CHLOROPHYLL

Ichimura, S. *et al.*, Japan Kokai, 74 86 512, 1974
Chlorophyl adsorbed on clay, or powdered unicellular green algae (chlorella) can be caused to explode by focussed irradiation from a powerful ruby laser.
See other IRRADIATION DECOMPOSITION INCIDENTS

CLATHROCHELATED METAL PERCHLORATES

Goedeken, V. L., *Inorg. Synth.*, 1980, **20**, 89
In the tris(2,3-butanedione dihydrazone) complexes of e.g. iron(II), nickel or cobalt(II or III) salts, the metal atom is effectively enclosed in an open ended chelating cylinder. The end of the cylinder can be closed by treating the complex with acidified aqueous formaldehyde, when at each end of the cylinder the 3 amino groups are converted to a hexahydrotriazine ring to give the clathrochelate salt. When the metal salts are perchlorates (and the formaldehyde is acidified with perchloric acid), the products must be regarded as treacherously unstable, like other perchlorate salts containing oxidisable matter, with avoidance of heating either the solids or the conc. solutions.

Individually indexed compounds are:
5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo[8.8.4.$1^{3,17}$.$1^{8,12}$]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22}cobalt(II) perchlorate, 3762
5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo[8.8.4.$1^{3,17}$.$1^{8,12}$]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22}iron(II) perchlorate, 3763

5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo[8.8.4.1^{3,17}.1^{8,12}]tetracosa-4,6,13,15,19,21-hexaene-*N*^{4},*N*^{7},*N*^{13},*N*^{16},*N*^{19},*N*^{22}nickel(II) perchlorate, 3764

POLYAZACAGED METAL PERCHLORATES

TETRAAZAMACROCYCLANEMETAL PERCHLORATES

See AMMINEMETAL OXOSALTS, [14] DIENE-N_4 COMPLEXES

CLEANING BATHS FOR GLASSWARE

Stahr, H. M. *et al., Anal. Chem.*, 1982, **54**, 1456A

As a safer and cheaper alternative to the use of sulfuric acid—dichromate mixtures (chromic acid, and of the hazardous nitric acid—ethanol, or sulfuric acid—permanganate mixtures), a sulfuric acid—ammonium persulfate bath is recommended as long-lasting and economical. However, any such oxidant mixture should be used with caution, and only when necessary. In the absence of significant adherent residues on glassware, one of the proprietary detergent formulations should give adequate cleaning, except perhaps for the most rigorous surface chemistry or trace analysis requirements.

See Chromic acid

Nitric acid: Alcohols (reference 2), 4430

Nitric acid: Glassware, 4430

Potassium permanganate: Sulfuric acid, etc. (references 2,3), 4642

See also PLANT CLEANING INCIDENTS

COAL

1. Rigsby, L. S., *J. Coal Qual.*, 1983, **2**(2), 16—20
2. Grossman, S. L. *et al., Coal Sci. Technol.* 1995, 24(Coal Sci. Vol. I) , 469, 473.
3. Grossman, S. L. *et al., Erdöl, Erdgas, Köhle*, 1996, **112**(7/8), 322
4. Marzec, A., *Chem. Abs.*, 1997, **127**, 164191e
5. Czajkowska, S. et al., *Karbo*, 2004, **49**(3), 122; *Chem. Abs.*, 2005, **142**, 264088e

All aspects of self-heating of coal during storage and transportation are considered, and the main factors are identified as temperature, rank, particle size, moisture and pyrites contents [1]. Although explosions are always attributed to methane, in fact bituminous coal emits hydrogen during warm storage by an oxidative decomposition mechanism, which can be a danger if ventilation is poor [2,3,4]. It is considered that explosive levels of hydrogen (easier ignited than is methane) can also be formed in mine galleries [5].

Sodium carbonate

See AUTOIGNITION TEMPERATURE (reference 7)

See also SELF-HEATING AND IGNITION INCIDENTS

COMMERCIAL ORGANIC PEROXIDES C—OO—

1. Boyars, C., *AD Rept. No. 742770*, Richmond (Va.), USNTIS, 1972
2. Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345—351
3. Leleu, *Cahiers*, 1980, (99), 279

4. Gehrke, H., *Zentr. Arbeitsmed. Arbeitsschutz*, 1977, **27**, 7—10
5. Venable, E., *Chem. Eng. News*, 1982, **60**(42), 94
6. Stull, 1977, 21
7. Wagle, U. D. *et al., Safety in Polyethylene Plants*, 1978, **3**, 62—68
8. Nakagawa, S., *Chem. Abs.*, 1979, **91**, 210654
9. de Groot, J. J. *et al., Runaway Reactions*, 1981, Paper 3/V, 1—17
10. de Groot, J. J. *et al., Ind. Eng. Chem., Proc. Des. Dev.*, 1981, **20**, 131—138
11. Mohan, V. K. *et al., J. Haz. Mat.*, 1982, **5**, 197—220
12. Fisher A., Ger. Offen., 2 637 940, 1978
13. *NFPA 43B*, Quincy (Ma), Natl. Fire Prot. Assocn., 1986

This group of compounds is widely used in industry as a radical source for initiation of polymerisation. They are available from several manufacturers in a very wide range of formulations in various diluents to reduce operational hazards. These were classified into 6 hazard levels and of the many materials available, the first list below of 6 compounds (all dry and unformulated except for that suffixed *, which is water-wetted) were included in the highest risk category. This specified the material as being sensitive to friction or mechanical shock equivalent to the dissipation of 1kg m or less of energy within the sample.

Existing and proposed methods of evaluating transportation hazards of organic peroxides exposed to impact, explosive shock or thermal surge stimuli were reviewed, and a hazard classification system proposed [1]. Commercial 2-butanone peroxide ('MEK peroxide') as a 40% solution in dimethyl phthalate was previously thought to be safe in normal storage or transport situations, but several road- and rail-tanker explosion incidents showed evidence of detonation. Application of steady-state thermal explosion theory allowed the prediction of critical mass and induction period in relation to temperature in bulk storage. The critical mass seems likely to have been attained in some of the incidents [2]. MEK peroxide diluted with mixed phthalate—phosphate esters and mixed with powdered charcoal gave accelerated decomposition above 35—40°C, with thick fumes [3]. (Catalysis by trace metals in the charcoal seems a likely factor). This peroxide is also used as a hardener in on-site production of polyester—concrete structural elements, and a violent explosion occurred which was attributed to incorrect storage conditions [4]. MEK peroxide is, of course, also an oxidant and will ignite acetone or other combustibles on contact, and may lead to explosion [5]. The result of calculations of the exothermic potential from thermal decomposition of neat MEK peroxide (Q = 218.5 kJ/mol, 1.79 kJ/g, leading to adiabatic product gas temperature of 832°C and a peak pressure of 32 bar) is related to the effects of a catastrophic transportation incident involving 17 t of mixed peroxides initiated by a small MEK peroxide fire [6].

A method was developed for the large-scale testing of the decomposition characteristics of commercial peroxides held in closed vessels of 2—120 l capacity fitted with bursting disks and temperature/pressure recording facilities. The results on *tert*-butyl peroxypivalate and *tert*-butyl peroxy-2-ethylhexanoate suggest that adequate pressure relief vents can be designed based on a constant area per unit volume of container [7]. The course and rate of pressure development when 20 organic peroxides were heated in a new pressure vessel test appear to offer a better assessment of potential hazards and pressure-relief requirements [8]. Thermal phenomena involved in the self-heating decomposition processes of organic peroxides have been investigated under isothermal, adiabatic and temperature-scanning conditions. A new rapid test method had been developed for assessing the effect of impurities upon stability [9]. Both simulated and experimental investigations of worst probable hazards likely from exothermic decomposition of bulk tanks (10 m^3) of commercial organic peroxides are described, and emergency procedures formulated [10]. A range of 6 commercial organic peroxides and hydrogen peroxide was screened using a variety of tests and a simplified classification of peroxides into 3 groups is proposed [11]. The use of expanded sodium borate as a carrier for organic peroxides is claimed to improve resistance to fire and detonation, and allows their safe use as catalysts, especially in aqueous systems [12]. A US National Fire Code covers requirements for safe storage of commercial formulated mixtures [13].

Individually indexed commercial peroxides are:
Acetyl cyclohexanesulfonyl peroxide, 3028
Bis(1-hydroperoxycyclohexyl) peroxide, 3550
Bis(2,4-dichlorobenzoyl) peroxide, 3617
Bis(2-hydroperoxy-2-butyl) peroxide, 3073
Bis(3-carboxypropionyl) peroxide, 2985
O—O-tert-Butyl hydrogen monoperoxymaleate, 3010
Diisopropyl peroxydicarbonate, 3029
1-Hydroperoxy-1′-hydroxydicyclohexyl peroxide, 3549
2-Phenyl-2-propyl hydroperoxide, 3160
See CYCLIC PEROXIDES, RADICAL INITIATORS

COMPLEX ACETYLIDES $K_m[M(C{\equiv}C)_n]$

1. Bailar, 1973, Vol. 4, 810
2. Nast, R. *et al., Chem. Ber.*, 1962, **95**, 1470—1483
3. Nast, R. *et al., Z. Anorg. Chem.*, 1955, **279**, 146—156

The title salts, where M is Cr(III), Co(II or III), Cu(0 or I), Au(I), Fe(II or III), Mn(II or III), Ni(0 or II), Pd(0), Pt(0 or II) or Ag(I) are frequently explosive [1], several of the analogous sodium salts being similar. A series of dialkynyl- palladates and -platinates [2] and a tetraalkynylnickelate [3] are pyrophoric, while other tetraalkynylnickelates are explosive [3]. Most react violently with water. Individually indexed compounds are:

* Bis(trimethylphosphine)nickel(0)—acetylene complex, 3087
Potassium bis(phenylethynyl)palladate(2—), 3692
Potassium bis(phenylethynyl)platinate(2—), 3693
Potassium bis(propynyl)palladate, 2301
Potassium bis(propynyl)platinate, 2302
Potassium diethynylpalladate(2—), 1390
Potassium diethynylplatinate(2—), 1391
Potassium hexaethynylcobaltate(4—), 3440
Potassium hexaethynylmanganate(3—), 3442
Potassium tetraethynylnickelate(2—), 2891
Potassium tetraethynylnickelate(4—), 2892
Potassium tetrakis(propynyl)nickelate(4—), 3507

* Potassium tricarbonyltris(propynyl)molybdate(3—), 3464
Sodium hexakis(propynyl)ferrate(4—), 3753
See other ACETYLENIC COMPOUNDS

COMPLEX HYDRIDES $[MH_n],[EH_n]$

1. Gaylord, 1956
2. Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 1—13
3. Ashby, E. C., *Rept. AD-A057764*, Richmond (Va.), NTIS, 1978
4. Ashby, E. C., *J. Organomet. Chem.*, 1980, **200**, 1—10

This group of highly reactive compounds includes several which have found extensive use in preparative chemistry [1]. Properties and reactions of several covalent tetrahydroborates have been reviewed [2]. Preparation and properties of several new hydrides are given which are of interest as high-energy fuels in propellant systems [3,4]. Individually indexed compounds are:

* Aluminium dichloride hydride diethyl etherate, 0061
Aluminium tetrahydroborate, 0058
Beryllium tetrahydroborate, 0157
Beryllium tetrahydroborate—trimethylamine, 1333
Bis(cyclopentadienyl)niobium tetrahydroborate, 3318
Bis(dimethylaminoborane)aluminium tetrahydroborate, 1789
Caesium hexahydroaluminate(3—), 0067
Caesium lithium tridecahydrononaborate, 0194
Calcium tetrahydroborate, 0158
Cerium(III) tetrahydroaluminate, 0089
Copper(I) tetrahydroaluminate, 0068
* Diammineboronium tetrahydroborate, 0167
Disodium tridecahydrononaborate(2—), 0195
Hafnium(IV) tetrahydroborate, 0182
Heptakis(dimethylamino)trialuminium triboron pentahydride, 3669
Lithium dihydrocuprate, 4265
Lithium pentahydrocuprate(4—), 4267
* Lithium tetradeuteroaluminate, 0069
Lithium tetrahydroaluminate, 0075
Lithium tetrahydroborate, 0145
Lithium tetrahydrogallate, 4401
Magnesium tetrahydroaluminate, 0085
Manganese(II) tetrahydroaluminate, 0086
Potassium hexahydroaluminate(3—), 0077
Potassium tetrahydrozincate, 4511
Potassium trihydomagnesate, 4488
Silver hexahydrohexaborate(2—), 0027
Sodium dihydrobis(2-methoxyethoxy)aluminate, 2570
Sodium octahydrotriborate, 0177
Sodium tetradecahydrononaborate, 0196
Sodium tetrahydroaluminate, 0076

Sodium tetrahydroborate, 0147
Sodium tetrahydrogallate, 4402
* Tricyclopentadienyluranium tetrahydroaluminate, 3681
Uranium(III) tetrahydroborate, 0178
Uranium(IV) tetrahydroborate etherates, 0183
Zirconium(IV) tetrahydroborate, 0184
See also METAL HYDRIDES
See other NON-METAL HYDRIDES, REDUCANTS

COMPRESSED GASES

Crowl, D. A. *Plant/Oper. Progr.* 1992, **11**(2), 47

Since the whole theme of this book is concerned with unexpected or concealed sources of energy, it is relevant to reiterate that compressed gases may contain a large content of kinetic energy over and above that potentially available from chemical reaction energy possibilities for the gas. A procedure for calculating available kinetic energy from rupture of compressed gas containers is found in [1]. Compression heating, or just pressure, may explode many unstable gases, or combustible mixtures thereof, during only slight compression.

See GAS CYLINDERS

COMPUTATION OF REACTIVE CHEMICAL HAZARDS

1. Treweek, D. N. *et al., J. Haz. Mat.*, 1976, **1**, 173—189
2. Domalski, E. S. *et al., Proc. 4th Int. Symp. Transp. Haz. Cargoes*, 1975, USNTIS PB 254214
3. *CHETAH, Chemical Thermodynamic and Energy Release Evaluation Program*, Philadelphia, ASTM, 1975
4. Sherwood, R. M., *Chem. Brit.*, 1975, **11**, 417
5. Treweek, D. N. *et al., Ohio J. Sci.*, 1980, **80**(4), 160—166
6. Yoshida, T. *et al., Chem. Abs.*, 1981, **95**, 64605
7. Yoshida, T. *et al., Primary Evaluation of Incompatibility and Energy Release* in *Proc. 4th Symp. Chem. Problems. Conn. Stab. Explosives*, (Hansson, J., Ed.), Tokyo, 1976
8. Yoshida, T. *et al., Chem. Abs.*, 1983, **95**, 7923
9. Yoshida, T. *et al., Chem. Abs.*, 1982, **93**, 188632
10. Davies, C. A.. *et al.*, in *Chem. Process Haz. Rev.*, (Hoffmann, J. M. & Mason, D. C., eds.), ACS Symp. Ser. 274, Ch. 9, 81—90, 1985
11. Frurip, D. J. *et al., Plant/Oper. Progr.*.,1989, **8**(2), 100—104
12. Shanley, E. S. *et al., J Loss Prev. Process Ind.*, 1995, **8**(5), 261
13. Harrison, B. K., private communication, 1998

During past decades, several computational methods for predicting instability (or ‘self-reactivity’) and mutual reactivity (’other chemical reactivity’) have been developed and tested. These have been variously based on structural and calculated thermodynamic parameters, amplified in some cases with experimentally determined data, to produce hazard rating systems.

These methods were jointly evaluated for their ability to predict successfully instability in a range of compound types. It was concluded that the relationship between the parameters considered and chemical stability was too obtuse for conventional statistical analysis. However, application of pattern-recognition techniques to statistical analysis was more fruitful, and 13 of the more promising parameters were evaluated successfully. Total under- and over-estimation error was below 10% relative to generally accepted forms of consensus grading into the 3 stability categories of explosive, hazardous decomposition or polymerisation, and non-hazardous. The methods appear to have great potential in minimising hazards in storage, transfer and transportation of chemicals [1].

In an alternative assessment of the effectiveness of these computer programs, it was concluded that explosive power was over-emphasised in relation to the more practically important aspect of sensitivity to initiation, and many compounds were being indicated as hazardous when they were not. There was also no provision for considering polymerisation as a hazardous possibility, and there was little quantitative data on this. The parameter best correlating with material sensitivity is the bond-dissociation energy. It was recommended that regulations specifying the handling and transport of chemicals should be based on the concept of known self-reactivity of functional groups present (nitro, nitramine, peroxide, azide, etc.) [2].

One of the computer programs [3] is relatively simple to apply, and gives estimates of the maximum energy release possible for any covalent compound or mixture of compounds containing C, H, O, N, and up to 18 other specified elements. Reactions and products may be specified if known, but the only essential input from the user is the amount and structure of each compound involved, the latter expressed in terms of the number of standard groups or skeletal fragments present in the structure. The graded results serve as a screening guide to permit decisions on which reaction systems need more detailed and/or experimental investigation [4]. In view of the difficulties which attend the use of thermodynamic parameters to try to predict mutual reactivity possibilities between pairs of compounds (‘other chemical reactivity’), a computational method has been developed which combines two existing reactivity-ranking procedures (NAS hazard rating system, and Lewis acid—base rating) which gives results within a 10% error margin of the experimental results of the Dow binary hazard classification system (measurement of exotherm and gas evolution on mixing two typical components). It is intended to incorporate this refinement into the CHETAH program [5]. The early program was used fairly successfully to correlate the calculated maximum heat of decomposition for various types of explosive materials (nitrate esters, nitramines, nitroaromatics, formulated explosives, and organic peroxides) with their performance in various standard tests and the heat of decomposition determined by sealed-cell DSC. Correlation was fairly good across the range of comparisons [6].

The EITP (Evaluation of Incompatibility from Thermodynamic Properties) program was originally applied to reduce the possibilities of fires occurring in chemical stores situated in earthquake zones, through collapse of shelving and indiscriminate mixing of reactive chemicals from broken containers. The program calculates for mixtures of 2 or more chemicals the maximum reaction heat (MRH) which is possible, and the proportions necessary for this. Working from case histories of incidents it was then possible to set threshold values for MRH below which no ignition was likely, so that storage schedules to segregate any potentially reactive chemicals could be prepared and implemented [7]. A second revised version (REITP2) was prepared and evaluated against the results of various instrumental tests for purposes more closely related to specific chemical stability problems in explosives and chemical intermediates and products [8]. The REITP program is effective for initial estimation of the degree of hazard arising from decomposition of unstable materials, while the sealed-cell DSC procedure gives more detail on the course and likely consequences of decomposition [9].

A general account of how the CHETAH program may be applied to estimation of chemical hazards in relation to process research and development has been given [10]. Progressively enhanced and user-friendly versions of CHETAH, which give an overall hazard assessment and are capable of running on personal computers are available from ASTM [11]. Comments critical of the criteria used for hazard evaluation in the 1994 CHETAH program [12] led to amendments and enhancements incorporated in the 1998 Windows version. The pure compound physical properties databank has since been expanded from 400 to 1500 compounds and the number of structural Benson groups used in thermodynamic calculations to > 730. An additional criterion, the Calculated Maximum Adiabatic Reaction Temperature (CART) is incorporated. Input of drawn structures via the CHEMDRAW package, with automatic subsequent calculations, is imminent. The new Windows version 7.3 is expected in 1999 [13].

CHEMICAL STABILITY/REACTIVITY ASSESSMENT
EXOTHERMICITY
EXPLOSIBILITY (references 3—5)
MAXIMUM REACTION HEAT
See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

CONDUCTING POLYMERS

See PERCHLORATE-DOPED CONDUCTING POLYMERS

COOL FLAMES

1. Coffee, R. D., *Cool Flames*, Chapter 18, 323—338 in *Safety and Accident Prevention in Chemical Operations*, Fawcett, H. H. & Wood, W. S., (Eds.), New York, Wiley, 2nd edn., 1982
2. D'Onofrio, E. J., *Loss. Prev.*, 1980, **13**, 99—95
3. Kolodner, H. J. *et al., Proc. 3rd Intl. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 2, 345—355, SSCI, Basle, 1980
4. Baronnet, R. *et al., Oxid. Commun.*, 1983, **4**(1—4), 83—95
5. Coffee, R. D., *Loss Prev. Bull.*, 1988, (081), 19—23
6. Caron, M. *et al., J. Hazard. Mat.*, 1999, **65**(3), 233
7. Pekalski, A. A. *et al., J. Haz. Mat.*, 2002, **93**(1), 93

The complex and incompletely understood phenomena of cool flames and their close relationship with autoignition processes is discussed in considerable detail. As the temperature of mixtures of organic vapours with air is raised, the rate of autoxidation (hydroperoxide formation) will increase, and some substances under some circumstances of heating rate, concentration and pressure will generate cool flames at up to 200°C or more below their normally determined AIT. Cool flames (peroxide decomposition processes) are normally only visible in the dark, are of low temperature and not in themselves hazardous. However, quite small changes in thermal flux, pressure, or composition may cause transition to hot flame conditions, usually after some delay, and normal ignition will then occur if the composition of the mixture is within the flammable limits.

Conditions most conducive to transition from cool flame to hot ignition are those encountered during sudden loss of vacuum and ingress of air during (or soon after) high temperature vacuum distillation processes. Many of the unexplained cases of ignition during these or similar processing operations of organic materials may be attributable to this transition [1]. In a study of the relationships of cool flame temperature, autoignition temperature and ignition delay times of a series of glycols in several sizes of containing vessels, it was found that ethylene glycol shows extremely long delay times. The transition from cool flame to hot ignition was demonstrated experimentally under conditions simulating progressive vacuum failure during vacuum distillation [2]. The same phenomenon, observed when air was admitted during vacuum distillation of a mixture of triethylene glycol diacetate with 36% of acetic acid, was investigated experimentally prior to pilot scale preparation of the ester, when nitrogen rather than air was admitted to break vacuum [3]. A semi-empirical correlation between cool flame behaviour of an organic compound and structure has been developed, but further experimental work is necessary [4]. A brief account of the nature and significance of cool flames in relation to process safety is presented [5]. Flammability studies of methane air mixtures under pressure (2-46 bar) have shown cool flames at above 40% methane. The cool flame temperature was found to correlate with the upper explosion limit [6]. A review of cool-flame hazards is given; these include formation of peroxides[7].

For an example, *See* 2,2-Dimethoxypropane, 1895

See AUTOIGNITION INCIDENTS, AUTOXIDATION

COOLING BATHS

1. Anon., *Sichere Chemiearbeit*, 1992, **44**(6), 70; *Jahresbericht*, 1991, 72
2. Editors comment

A substantial explosion, followed by a fire causing fatal burns to the experimenter, occurred when working with butyllithium in tetrahydrofuran cooled by a propan-2-ol / solid carbon dioxide freezing bath. It was considered that the explosion might have been fueled by isopropanol vapour in air. This explanation was rejected since the alcohol should have been below its flash point. However, making up such cooling baths, containing flammable solvents, does disperse considerable quantities of vapour and mist, albeit carried by carbon dioxide, before the mix is fully cooled. There is a period of potential hazard, as there may be when the bath warms above the flash point once more [1]. Although needed to control exothermic reactions, cooling can be overdone. An overcooled semi-batch reaction (one in which one or more reagents is added slowly to the reaction mix, thereby limiting heat evolution) will accumulate unreacted reagent, which can then react uncontrollably when the reaction warms,

whether from increasing internal heat (reagent concentration usually controls rate of reaction) or because of cessation of cooling. The academic technique of mixing reagents at liquid nitrogen temperature, then allow to warm up, is an extreme example of this hazard, in batch form Many accidents of this origin, on both laboratory and industrial scale, are found in these pages [2].
See also MISTS

COPPER CHROMITE CATALYST $Cu_2O.Cr_2O_3$

Alcohols

Budniak, H., *Chem. Abs.*, 1975, **83**, 134493
Copper chromite catalyst, after use in high-pressure hydrogenation of fatty acids to alcohols, is pyrophoric, possibly owing to presence of some metallic copper and/or chromium. Separation of the catalyst from the product alcohols at 130°C in a non-inerted centrifuge led to a rapid exotherm and autoignition at 263°C.

Ammonium perchlorate

See Ammonium perchlorate: Catalysts (reference 2)
See other HYDROGENATION CATALYSTS

CORROSION INCIDENTS

1. Hammer, N. E., *Dangerous Prop. Ind. Mater. Rept.*, 1981, **1**(8), 2—7
2. Asakura, S. *et al., Chem. Abs.*, 1982, **96**, 147574
3. Maddison, T. E., *Loss Prev. Bull.*, 1987, (076), 31—38

Hazards created by corrosion involving consumer products, industrial installations, utility systems and dangerous wastes are reviewed [1]. Auto-accelerating corrosion reactions of copper components in acidic media which could lead to sudden plant failure have been studied [2]. Seven cases involving catastrophic failure of large glass-reinforced plastic (GRP) storage tanks are described, most stemming from corrosive attack of the GRP structural elements by the contained liquors, sometimes after failure of a polymeric liner. Plastics are not commonly considered to be subject to corrosive attack [3].

Some examples of these incidents are:
Aluminium, : Butanol, 0048
Aluminium, : Mercury(II) salts, 0048
Aluminium, : Metal nitrates, Sulfur, Water, 0048
Aluminium, : Water, 0048
Ammonium sulfide, : Zinc, 4572
Calcium chloride, : Zinc, 3917
Chlorine, : Aluminium, 4041
Chlorine, : Steel, 4041
Gallium, : Aluminium alloys, 4400
Magnesium chloride, : Air, Mild steel, Water, 4075
Magnesium, : Halocarbons, 4685
Magnesium, : Methanol, 4685
Magnesium, : Water, 4685

Mercury, : Metals, 4595
Methacrylic acid, 1525
Orthophosphoric acid, : Chlorides, Stainless steel, 4500
Potassium,(references 4—5a), 4640
Sodium sulfide, : Glass, 4805
Uranium, : Nitric acid, Trichloroethylene, 4917

COTTON

Oils

Anon., *Textil-Rundschau*, 1957, **12**, 273

Cotton waste in contact with fatty oils (especially of unsaturated character) is much more subject to self-heating and autoignition than animal fibres. Various factors affecting storage hazards of baled cotton, including the aggravating effects of moisture, are discussed. Mineral oils, though generally less subject to oxidative heating than vegetable oils, have also been involved in autoignition incidents

See CELLULOSE

COUMARONE—INDENE RESIN

The finely powdered resin is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

CRITICAL IGNITION TEMPERATURE

Kotoyori, T., J. *Loss Prev. Proc. Ind.*, 1989, **2**, 16—21

Materials of limited thermal stability may self-heat and eventually ignite through progressive accelerating decomposition if they are stored or processed above the critical ignition temperature (CIT). Knowledge of this is therefore essential for defining safe conditions for processing or storing such materials. Existing tests to determine this temperature involve a series of runs with adiabatic storage of samples at different (increasing) temperatures until ignition is observed. This temperature is not an absolute value, but depends on sample size and induction period allowed. In the BAM heat accumulation storage test, samples are the largest standard commercial package, amd the induction time is set at 7 days, the result being the self-accelerating decomposition temperature (SADT). Naturally, this test requires many kg of material to complete.

A new small-scale test has been developed which needs only a few g of thermally unstable material, which may be contained in an open cell version of the apparatus if aerobic processes are involved, otherwise in a closed cell apparatus, both with full temperature control and monitoring systems. Such materials may be divided into 2 types, depending on the behaviour of a sample after introduction into adiabatic storage at elevated temperature. The first type, which after attaining the adiabatic temperature shows a steady further increase in temperature in line with Frank-Kamenetski's thermal explosion theory, exhibit thermal combustion (TC) behaviour. In the second type, after adiabatic temperature has been reached, the sample shows a sudden rapid rate of rise, exhibiting autocatalytic (AC) behaviour as chain branching

and acceleration set in. Of 8 materials examined in this test, five showed TC behaviour (azoisobutyronitrile, dibenzoyl peroxide, dinitrosopentamethylene tetramine, 4,4′-oxybis(benzenesulfonylhydrazide) and calcium hypochlorite), while 3 showed AC behaviour (cellulose nitrate, dilauroyl peroxide and toluenesulfonylhydrazide). CIT values, largely comparable with the BAM results, are given in the individual entries:
Azoisobutyronitrile, 3006
Calcium hypochlorite, 3918
Dibenzoyl peroxide, 3632
Didodecanoyl peroxide, 3851
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1948
4,4′-Oxybis(benzenesulfonylhydrazide), 3519
4-Toluenesulfonylhydrazide, 2823
See entry DEFLAGRATION INCIDENTS, HIGH RATE DECOMPOSITION

CROWN ETHERS

As cyclic polyethers (polyethylene oxides), some of this group of aprotic complexing solvents may be subject to peroxidation, though no reports have been so far noted.
See 1,4,7,10,13,16-Hexaoxacyclooctadecane (‘18-Crown-6’)

Bromoform, Potassium hydroxide, etc.
See Bromoform: Cyclic polyethylene oxides, Potassium hydroxide

CRYOGENIC LIQUIDS

1. Zabetakis, M. G., *Safety with Cryogenic Fluids*, London, Heywood, 1967
2. *Safety Panel, British Cryogenics Council, Cryogenics Safety Manual — A Guide to Good Practice*, Oxford, Butterworth-Heinemann, 3rd edn., 1991
3. *Safety Problems in Handling Low-Temperature Industrial Fluids*, 1964, IChE Symp. papers, published in *Chem. Engr.*, 1965, **43**(185), CE7—10; (186), CE36—48
4. Bernstein, J. T., *Cryogenics*, 1973, **13**, 600—602
5. *B.S. Code of Practice*, BS 5429: 1976
6. Timmerhaus, K. D. *et al., Adv. Cryog. Eng. 1977*, 1978, **23**, 721—729
7. *Recommended Safety Precautions for Handling Cryogenic Liquids*, Crawley, Edwards High Vacuum, 1979
8. Ordin, P. M., *Liqu. Cryog.*, 1983, **1**, 1—57
9. Hofmann, M. J., *J. Chem. Educ.*, 1986, **63**(6), A149—150
10. Ryan, K. P. *et al., Microscope*, (Oxford), 1987, **147**, 337—340
11. Rouault, F. C., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 537—556, Heidelberg, ISSA, 1987
12. Currie, J. L., *Cryogenics*, 1988, **28**, 830—834
13. Anon., *Sichere Chemiearbeit*, 1997, **49**(1), 10

The monograph presents concisely in 6 chapters the principles of safety applicable to cryogenics, with safety data sheets for 15 cryogenic fluids [1]. The revised safety manual covers the operation and maintenance of plant for producing, storing and handling commercial gases which liquefy at low temperatures, and precautions in the use of these materials [2]. The symposium covered possible fire and explosion hazards in general terms, as well as in detail for liquid hydrogen, acetylene, natural gas, and a low-temperature nitrogen-washing process for ammonia synthesis gas [3]. Safety aspects of sampling and handling cryogenic liquids were reviewed [4] and the Code of Practice provides users of liquid oxygen, nitrogen, argon, natural gas, etc. with a basic appreciation of the problems associated with the small-scale use and storage of these materials [5]. Aspects of cryogenic systems involving physiological materials and high pressure are discussed [6], and a 16-page booklet briefly covers essential aspects of the title topic [7]. A review of safety in handling and use of cryogenic fluids includes 69 references [8], and safe practices in their laboratory use are presented [9].

In a review of the use of various cryogenic liquids for rapid freezing of biological specimens for cryo-sectioning, hazards attendant on the use of liquid propane and similar cryogens are discussed. Upon evaporation, the volume of mixture with air within the explosive range may be 14,000 times that of the volume of original liquid, and this may be a significant proportion of the free space in a confined work area. Precautions including the use of nitrogen blanketing, a fume cupboard, and adequate ventilation are discussed [10]. The use of a computer controlled interlocked interactive sequencing system to prevent mistakes in loading road tankers with cryogenic liquids is described [11]. The role of the Cryogenics Safety Manual (reference 2 above) as a training guide is discussed, and the major changes in the scheduled 1988 revision are highlighted [12].

A cryogenic storage vial frozen in liquid nitrogen exploded on rewarming to just above ambient temperature, injuring a worker. It is considered that liquid nitrogen seeped round the contracted and hardened seal, which resealed on warming. It is suggested caps be loosened immediately on removal from storage and (impractically?) that vials be filled to the brim, leaving no room for liquid gases [13].

Some examples of cryogens are:
† Hydrogen (Liquid), 4448
Nitrogen (Liquid), 4730
Oxygen (Liquid), 4826
† Propane, 1267
See Argon, : Liquid nitrogen
See also LIQUEFIED GASES

CRYSTALLINE HYDROGEN PEROXIDATES

1. Castrantas, 1965, 4
2. Emeléus, 1960, 432
3. Kirk-Othmer, 1966, Vol. 11, 395
4. Mellor, 1971, Vol. 8, Suppl. 3, 824
5. Editor's comments, 1999
6. Jones, D. P. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 2526—2532

Many compounds will crystallise out with hydrogen peroxide in the crystal lattice, analogous to crystalline hydrates. A few (some of which are listed below) sequester

the peroxide preferentially from water. These complexes represent a form of concentrated hydrogen peroxide distributed at a molecular level, which may react violently in close contact (grinding or heating) with oxidisable materials [1]—[4]. If the host is itself oxidisable, this molecular distribution makes detonability highly probable [5]. Some examples of true peroxodicarbonates (MOCO.OOCO.OM) have been prepared, but they do not behave as oxidants, immediately hydrolysing in water to hydrogen peroxide [6]. Individually indexed compounds are:
1,4-Diazabicyclo[2.2.2]octane hydrogen peroxidate, 2468
Potassium citrate tri(hydrogen peroxidate), 2251
Potassium fluoride hydrogen peroxidate, 4294
Sodium borate hydrogen peroxidate, 0154
Sodium carbonate hydrogen peroxidate, 0550
Sodium pyrophosphate hydrogen peroxidate, 4810
Triethylamine hydrogen peroxidate, 2565
Urea hydrogen peroxidate, 0475
See Hydrogen peroxide: Nitric acid, Thiourea
See AMINE OXIDES

CUBANES $C_8H_{8-n}X_n$

1. Eaton, P. E., *Angew. Chem. (Int.)*, 1992, **31**(11), 1421
2. Eaton, P., *Chem. Abs*, 1993, **119**, 75812
3. Schmitt, R. J. *et al., Chem. Abs.* 1994, **121**, 112782
4. Piermarini, G. J. *et al., Propellants, Explos., Pyrotech., 1991,* **16**(4), 188
5. Su, Z. *et al., Proc. Int. Pyrotech. Semin.*, 1991, (17th) Vol. 1, 224
6. Eaton, P. E. *et al., J. Amer. Chem. Soc.*, 1997, **119**(41), 9591

All cubanes are high energy materials and should be handled with due precautions for potential explosives [1]. The ring system has almost 700 kJ/mol strain energy (more, per unit weight, than the detonation energy of TNT) and is under study as a basis for high power explosives [2,3]. Cubane itself explodes spontaneously at 3 GPa pressure, the 1,4-dinitro derivative not until > 7 GPa [4]. The slightly less strained homocubanes are also studied as explosives [5]. Cubane acyl azides are sensitive and powerful primary explosives; they should be handled only in dilute solution [6]. Individual cubanes are:
1,4-Dinitropentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, 2913
Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, 2933
Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,2-dicarboxylic acid, 3255
See other STRAINED-RING COMPOUNDS

CYANIDES CN^-

Hypochlorites

1. Wallace, V., *Chem. Eng. News*, 1978, **56**(4), 3
2. Kirk-Othmer, 3rd Edn., Vol. 7, 322

Care is necessary in using hypochlorite solutions to destroy cyanide wastes by oxidation to cyanates. This reaction goes readily, even at high pH, but the secondary oxidation of cyanate to nitrogen and carbon dioxide is very pH dependent. This is slow at pH 11 but runs away at 10—10.3, with subsequent sudden release of nitrogen gas. Disposal operations should be conducted to avoid the combination of high pH, excess of hypochlorite and moderate or high concentrations [1]. On the other hand, pH above 9 is recommended to avoid nitrogen trichloride formation [2]. Addition of 0.5 ml of cyanide solution to 5 ml of stirred hypochlorite destroyed a gas meter with the violent gas evolution [1].

See Nitrogen trichloride
See METAL CYANIDES (AND CYANO COMPLEXES)
See other GAS EVOLUTION INCIDENTS

CYANO COMPOUNDS —C≡N, C≡N⁻

Metal cyanides are readily oxidised and those of some heavy metals show thermal instability. The covalent cyano group is endothermic, and hydrogen cyanide and many organic nitriles are unusually reactive under appropriate circumstances, and *N*-cyano derivatives are reactive or unstable. The class includes the groups and individually indexed compounds are:

† Acetonitrile, 0755
† Acrylonitrile, 1104
∗ Allyl isothiocyanate, 1467
3-Aminopropiononitrile, 1208
∗ Ammonium thiocyanate, 0477
Azidoacetonitrile, 0710
2,2′-Azobis(2,4-dimethylvaleronitrile), 3661
Azoisobutyronitrile, 3006
2,2′-Azoisovaleronitrile, 3339
Bis(2-cyanoethyl)amine, 2391
Bis(acrylonitrile)nickel(0), 2305
∗ 1,3-Bis(isocyanomethyl)benzene, 3251
∗ Bis(trifluoromethyl)cyanophosphine, 1050
∗ Butane-1,4-diisocyanate, 2369
† Butyl isocyanate, 1925
† Butyronitrile, 1558
Caesium cyanotridecahydrodecaborate(2—), 0515
Calcium cyanamide, 0315
2-Carbamoyl-2-nitroacetonitrile, 1113
∗ Carbonyl diisothiocyanate, 1338
2-Chloro-1-cyanoethanol, 1127
† 2-Chloroacrylonitrile, 1071
2-Chlorobenzylidenemalononitrile, 3232
4-Chlorobutyronitrile, 1483
∗ 4-Chlorophenyl isocyanate, 2644
∗ Chlorosulfonyl isocyanate, 0323
Cyanamide, 0403
2-Cyano-1,2,3-tris(difluoroamino)propane, 1428
3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2626
N-Cyano-2-bromoethylcyclohexylamine, 3172

2-Cyano-2-propanol, 1561
1-Cyano-2-propen-1-ol, 1463
2-Cyano-2-propyl nitrate, 1502
4-Cyano-3-nitrotoluene, 2912
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2664
Cyanoacetic acid, 1110
Cyanoacetyl chloride, 1072
* Cyanoborane oligomer, 0392
Cyanocyclopropane, 1459
Cyanodiazoacetyl azide, 1342
2-Cyanoethanol (3-Hydroxypropanenitrile), 1177
Cyanoform, 1379
Cyanoformyl chloride, 0597
Cyanogen bromide, 0312
Cyanogen chloride, 0322
Cyanogen fluoride, 0337
Cyanoguanidine, 0809
Cyanohydrazonoacetyl azide, 1080
* Cyanonitrene, 0537
† 1-Cyanopropene, 1460
† 3-Cyanopropene, 1461
* 3-Cyanopropyne, 1412
† Cyanotrimethylsilane, 1659
Diazidomalononitrile, 1343
Diazidomethylenecyanamide, 1013
2,3-Diazidopropiononitrile, 1118
Diazomalononitrile, 1340
2-Diazonio-4,5-dicyanoimidazolide, 2044
* 1,2-Dibromo-1,2-diisocyanatoethane polymers, 1383
* Dibutylthallium isocyanate, 3187
1,4-Dicyano-2-butene, 2304
† Dicyanoacetylene, 1795
Dicyanodiazene, 1001
Dicyanofurazan, 1797
Dicyanofurazan *N*-oxide, 1798
† Dicyanogen, 0992
* Dicyanogen *N,N′*-dioxide, 0994
Dicyanoiodonium triflate, 1045
(Difluoroamino)difluoroacetonitrile, 0626
* 1,6-Diisocyanatohexane, 3003
* Diisocyanatomethane, 1076
* 2,4-Diisocyanatotoluene, 3111
* 1,4-Diisocyanobutane, 2365
* 1,5-Diisocyanopentane, 2821
* Disodium dicyanodiazenide, 1002
* Disulfur thiocyanate, 0999

* 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,5-dihydro-3*H*-pyrazole, 3605
Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2352
Ethyl cyanoacetate, 1883
* Ethyl isocyanide, 1174
Fumarodinitrile, 1393
* Germanium isocyanate, 1373
Glutarodinitrile, 1864
Glycolonitrile, 0757
* Hexaethyltrialuminium trithiocyanate, 3688
† Isobutyronitrile, 1560
* Isocyanoamide, 0406
* 2-Isocyanoethyl benzenesulfonate, 3137
* Isopropylisocyanide dichloride, 1556
Malononitrile, 1075
Mercaptoacetonitrile, 0763
Methyl 3,3-diazido-2-cyanoacrylate, 1818
† Methyl isocyanate, 0758
* Methyl isocyanide, 0756
* Methyl isocyanoacetate, 1466
* 1-Naphthyl isocyanate, 3384
2-Nitrobenzonitrile, 2658
Nitrosyl cyanide, 0538
* Oxopropanedinitrile, 1337
Perfluoro-*N*-cyanodiaminomethane, 0633
Phenylacetonitrile, 2929
2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile), 3616
* 2-Phenylethyl isocyanate, 3133
* Phosphorus tricyanide, 1339
* Phosphoryl dichloride isocyanate, 0326
† Pivalonitrile, 1923
† Propiononitrile, 1175
Silver 3-cyano-1-phenyltriazen-3-ide, 2666
Succinodinitrile, 1429
Sulfinylcyanamide, 0539
* Sulfur thiocyanate, 0998
* Tetraacrylonitrilecopper(I) perchlorate, 3504
Tetracyanoethylene, 2625
Tetracyanooctaethyltetragold, 3808
Tetramethylsuccinodinitrile, 3002
* Thiocarbonyl azide thiocyanate, 1007
* Thiocyanogen, 0997
Trichloroacetonitrile, 0604
Trinitroacetonitrile, 1005
* Vinyl isocyanide, 1106

3-CYANOTRIAZENES

DIISOCYANIDE LIGANDS

METAL CYANIDES(AND CYANO COMPLEXES)

3-CYANOTRIAZENES N=N—N(C≡N)

Bretschneider, H. *et al., Monatsh.*, 1950, **81**, 981

Many aromatic 3-cyanotriazenes are shock-sensitive, explosive compounds.

See other HIGH-NITROGEN COMPOUNDS, TRIAZENES

CYCLIC PEROXIDES

1. Swern, 1970, Vol. 1, 37; 1972, Vol. 3, 67, 81
2. Nixon, J. R. *et al., J. Org. Chem.*, 1978, **43**, 4052, footnote 18

Generally produced *inter alia* during peroxidation of aldehydes or ketones, the lower members are often violently explosive. Dimeric and trimeric ketone peroxides are the most dangerous group of organic peroxide, exploding on heating, touching or friction [1]. Some bromo-and hydrido-cyclic peroxides exploded repeatedly during micro-analytical combustion [2]. Individually indexed compounds are:

2,2′-Biphenyldicarbonyl peroxide, 3624
1,6-Di(4′-tolyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3790
1,6-Diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane, 2470
2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane, 2291
4,5-Dichloro-3,3,4,5,6,6-hexafluoro-1,2-dioxane, 1351
3,6-Dichloro-3,6-dimethyltetraoxane, 1488
2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane, 2332
3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 3047
3,6-Dimethyl-1,2,4,5-tetraoxane, 1620
1,4-Dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene, 2382
2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide, 2381
Dimethyldioxirane, 1223
7,8-Dioxabicyclo[4.2.2]-2,4,7-decatriene, 2950
cis-1,4-Dioxenedioxetane, 1533
3,6-Dioxo-1,2-dioxane, 1441
3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane, 3540
endo-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene, 2329
1,4-Epidioxy-1,4-dihydro-6,6-dimethylfulvene, 2979
1,4-Epidioxy-2-*p*-menthene, 3341
9,10-Epidioxyanthracene, 3623
3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane, 3189
3-Methoxy-3-methyl-5,6-benzo-6*H*-1,2-dioxin, 3307
3-Methoxy-4-methyl-5,6-benzo-6*H*-1,2-dioxin, 3308
1-(*cis*-Methoxyvinyl)-1,4-endoperoxy-2,5-cyclohexadiene, 3147
3-Methyl-1,2,4-trioxolane, 1231
Methyltrifluoromethyldioxirane, 1099
3- or 4-Methoxy-5,6-benzo-6*H*-1,2-dioxin, 3148
4a,8a,9a,10a-Tetraaza-2,3,6,7-tetraoxaperhydroanthracene, 2472
3,3,4,5-Tetrachloro-3,6-dihydro-1,2-dioxin, 1386

3,3,6,6-Tetrakis(bromomethyl)-9,9-dimethyl-1,2,4,5,7,8-hexoxonane, 3167
3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 2512
7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione, 3343
Tetramethyl-1,2-dioxetane, 2502
3,6,9-Triethyl-1,2,4,5,7,8-hexoxonane, 3190
Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane, 3686
See Hydrogen peroxide: Ketones, Nitric acid
See also COMMERCIAL ORGANIC PEROXIDES, DIOXETANES

CYCLOPROPANES

Although the cyclopropane ring is kinetically more stable than the other three-membered rings given entries it is thermodynamically just as strained. Examples will be found in Part 1 where such part-structures definitely contribute to explosibility, even if not the sole cause.
See STRAINED-RING COMPOUNDS

DEFLAGRATION INCIDENTS

Some incidents involving deflagration may be found under:
  Ammonium dichromate, 4240
  4-Chloronitrobenzene, 2135
  1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3695
  Hydroxylaminium sulfate, 4570
  4-Nitrobenzoic acid, 2691
  2-Nitrosophenol (1,2-Benzoquinone monoxime), 2256
  Sodium 3-nitrobenzenesulfonate, 2177
See entry CRITICAL IGNITION TEMPERATURE, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION (reference 3)

DEFLAGRATION TO DETONATION

Chatrathi, K. *et al., Process Safety Progr.*, 1996, **15**(4), 237
A study of deflagration to detonation transition in pipes, for gas/air and dust mixtures, has been made and reported. Obviously it depends upon the exact mixture, but departures from the straight and narrow generally facilitate this transition from slight to seriously destructive over-pressures.
See also DUST EXPLOSION INCIDENTS, GEOMETRY OF VESSELS AND PIPEWORK, VAPOUR CLOUD EXPLOSIONS

DEVARDA'S ALLOY **Cu—Al—Zn**

1. Cameron, W. G., *Chem. & Ind.*, 1948, 158
2. Chaudhuri, B. B., *Chem. & Ind.*, 1948, 462

The analytical use of the alloy to reduce nitrates is usually accompanied by the risk of a hydrogen explosion, particularly if heating is effected by flame. Use of a safety screen and flameless heating, coupled with displacement of hydrogen by an inert gas,

are recommended precautions [1]. The explosion was later attributed to gas pressure in a restricted system [2].
See other ALLOYS, GAS EVOLUTION INCIDENTS

DIACYL PEROXIDES $RCO.OOCO.R, RSO_2.OOSO.R_2$

1. Swern, 1970, Vol. 1, 70
2. Mageli, O. L. *et al.*, US Pat. 3 956 396, 1976
3. Fujimori, K., *Org. Peroxides, Chichester, John Wiley,* 1992, 319

Most of the isolated diacyl (including sulfonyl) peroxides are solids with relatively low decomposition temperatures, and are explosive, sensitive to shock, heat or friction. Several, particularly the lower members, will detonate on the slightest disturbance. Autocatalytic (self-accelerating) decomposition, which is promoted by tertiary amines, is involved [1]. Solvents suitable for preparation of safe solutions of diacetyl, dipropionyl, diisobutyryl and di-2-phenylpropionyl peroxides are disclosed [2]. The class is reviewed, including hazards and safety measures [3]. Cyclic diacyl peroxides are more stable, but scarcely to be trusted. Individually indexed compounds are:

Acetyl cyclohexanesulfonyl peroxide, 3028
2,2′-Biphenyldicarbonyl peroxide, 3624
Bis(2,4-dichlorobenzoyl) peroxide, 3617
* Bis(2-azidobenzoyl) peroxide, 3621
Bis(3,4-dichlorobenzenesulfonyl) peroxide, 3439
Bis-3-(2-furyl)acryloyl peroxide, 3633
Bis(3-carboxypropionyl) peroxide, 2985
Bis(4-chlorobenzenesulfonyl) peroxide, 3452
Bis(bromobenzenesulfonyl) peroxide, 3447
Bis(fluoroformyl) peroxide, 0621
Bis(trichloroacetyl) peroxide, 1357
Bis(trifluoroacetyl) peroxide, 1363
Di-1-naphthoyl peroxide, 3825
Di-2-furoyl peroxide, 3239
Di-2-methylbutyryl peroxide, 3348
Di-3-camphoroyl peroxide, 3801
Di-4-toluenesulfonyl peroxide, 3649
Diacetyl peroxide, 1532
Dibenzenesulfonyl peroxide, 3493
Dibenzoyl peroxide, 3632
Dicrotonoyl peroxide, 2981
Dicyclohexylcarbonyl peroxide, 3660
Didodecanoyl peroxide, 3851
Dihexanoyl peroxide, 3548
Diisobutyryl peroxide, 3027
Diisopropyl peroxydicarbonate, 3029
Dimethanesulfonyl peroxide, 0927
3,6-Dioxo-1,2-dioxane, 1441

Dipropionyl peroxide, 2436
Dipropyl peroxydicarbonate, 3030
Peroxodisulfuryl difluoride, 4322
Phthaloyl peroxide, 2895
Potassium benzenesulfonylperoxosulfate, 2250
Potassium *O*—O-benzoylmonoperoxosulfate, 2680
* *O*-Trifluoroacetyl-*S*-fluoroformyl thioperoxide, 1047
See PEROXIDES, PEROXYCARBONATE ESTERS

DIALKYL HYPONITRITES RON=NOR

1. Partington, J. R. *et al., J. Chem. Soc.*, 1932, **135**, 2593
2. Mendenhall, G. D. *et al., J. Amer. Chem. Soc.*, 1982, **104**, 5113
3. Ogle, C. A. *et al., J. Org. Chem.*, 1983, **48**, 3728—3733

The violence of the explosion when the ethyl ester was heated at 80°C was not so great as reported previously. The propyl and butyl esters explode if heated rapidly, but decompose smoothly if heated gradually [1]. Dialkyl hyponitrites with alkyl groups below C_6 are shock-sensitive [2]. The shock-sensitivity decreases with increasing MW, and it was not possible to detonate esters above C_6. The aryl esters were insensitive and the alkyl esters became so on dilution with solvent [3]. Individually indexed compounds are:

Dibutyl hyponitrite, 3064
trans-Di-*tert*-butyl hyponitrite, 3065
Diethyl hyponitrite, 1684
Diisopropyl hyponitrite, 2533
Dimethyl hyponitrite, 0909
Dipropyl hyponitrite, 2534
See related AZO COMPOUNDS

DIALKYLMAGNESIUMS R_2Mg

Alcohols, Ammonia, Carbon dioxide or Water

Sidgwick, 1950, 233

This series, either as the free alkyls or their ether complexes, is extremely reactive, igniting in air or carbon dioxide and reacting violently or explosively with alcohols, ammonia or water. Individually indexed compounds are:

Diethylmagnesium, 1681
Dimethylmagnesium, 0904
Diphenylmagnesium, 3476
See other ALKYLMETALS

DIALKYL PEROXIDES ROOR

1. Castrantas, 1965, 12
2. Swern, 1970, 1, 38, 54
3. Davies, 1961, 75
4. Uetake, K. *et al., Bull. Chem. Soc. Japan*, 1979, **52**, 2136

The high and explosive instability of the lower dialkyl peroxides decreases rapidly with increasing chain length and degree of branching, the di-*tert*-alkyl peroxides being amongst the most stable of the group [1,2]. Though many 1,1-bis(peroxides) have been reported, few have been purified because of the higher explosion hazards, compared with the monofunctional peroxides [3]. Samples of 4 pure liquid dialkyl peroxides were thermally decomposed in TGA—DSC equipment to provide information for hazard prevention [4]. Individually indexed compounds are:

* Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide, 3560
2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3703
2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3705
† Di-*tert*-butyl peroxide, 3069
* 2,2-Di(*tert*-butylperoxy)butane, 3559
Diethyl peroxide, 1693
Dimethyl peroxide, 0919
Dipropyl peroxide, 2542
Ethyl methyl peroxide, 1278
See PEROXIDES

DIALKYLZINCS R_2Zn

1. Sidgwick, 1950, 266
2. Noller, C. R., *J. Amer. Chem. Soc.*, 1929, **51**, 597
3. Houben-Weyl, 1973, Vol. 13.2a, 560, 576

The dialkylzincs up to the dibutyl derivatives readily ignite and burn in air. The higher alkyls fume but do not always ignite [1]. During preparation of dialkylzincs, reaction of the copper—zinc alloy with mixed alkyl bromides and iodides must begin (exotherm, often after a long induction period), before too much halide mixture is added, or violent explosions may occur [2]. Reactions with water may be explosive [3].
See other INDUCTION PERIOD INCIDENTS

Acyl halides
Houben-Weyl, 1973, Vol. 13.2a, 781
Too-fast addition of acyl halides during preparation of ketones may lead to explosive reactions.

Alkyl chlorides
Noller, C. R., *J. Amer. Chem. Soc.*, 1929, **51**, 599
During interaction to give hydrocarbons, too much chloride must not be added before reaction sets in (induction period), or explosions may occur.
See other INDUCTION PERIOD INCIDENTS

Methanol
Houben-Weyl, 1973, Vol. 13.2a, 855
Contact of the neat liquids with uncooled methanol is explosively violent and leads to ignition. For analysis, ampouled samples of dialkylzincs must first be frozen in liquid nitrogen before being broken under methanol—heptane mixtures at —60°C.

Individually indexed compounds are:
  Dibutylzinc, 3074
  Diethylzinc, 1712
  Diisobutylzinc, 3075
  Diisopentylzinc, 3365
  Dimethylzinc, 0931
  Dipropylzinc, 2546
See Zinc ethoxide: Nitric acid
See other ALKYLMETALS

1,3-DIAZA-2-BORACYCLOALKANES

Alcohols

Merriman, J. S. *et al., Inorg. Synth.*, 1977, **17**, 165

These heterocycles react readily with protic solvents, and alcohols in particular may occasionally cause explosive solvolysis reactions.

See related BORANES

DIAZIRINES

1. Schmitz, E. *et al., Org. Synth.*, 1965, **45**, 85
2. Liu, M. T. H., *Chem. Eng. News*, 1974, **52**(36), 3
3. Terpinski, J. *et al., Magn. Reson. Chem.*, 1987, **25**, 923—927

Diazirine and several of its 3-substituted homologues, formally cyclic azo compounds, are explosive on heating or impact [1]. The shock-sensitivity of all diazirine compounds and the inadvisability of their handling in the undiluted state have again been stressed [2]. In a description of the synthesis of 27 3-(4-substituted)-halodiazirines, the need is stressed to handle the compounds at below 30°C to prevent thermal decomposition, or, for the pure compounds, explosion [3].

Individually indexed compounds are:
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2641
3-Chloro-3-methoxydiazirine, 0730
3-Chloro-3-methyldiazirine, 0729
3-Chloro-3-trichloromethyldiazirine, 0607
3-Chloro-3-trifluoromethyldiazirine, 0590
Chloro-(4-methoxyphenyl)diazirine, 2923
Diazirine, 0404
Diazirine-3,3-dicarboxylic acid, 1077
Difluorodiazirine, 0341
Dipotassium diazirine-3,3-dicarboxylate, 1336
3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine, 0627
3-Methyldiazirine, 0804
3,3-Pentamethylenediazirine, 2416
Potassium hydrogen diazirine-3,3-dicarboxylate, 1065
3-Propyldiazirine, 1589

Spiro(homocubane-9,9′-diazirine) (Spiro[3**H**-diazirine-3,9¯pentacyclo [4,3,0,0^{2,5}0^{3,8}0^{4,7}]nonane], 3121
See related AZO COMPOUNDS

DIAZOAZOLES

1. Hui, H. *et al., Tetrahedron Lett.*, 1982, **23**, 5115—5118
2. Magee, W. L. *et al, J. Org. Chem.*, 1987, **52**, 5538—5548

Four 4-diazo-1,2,3-triazole derivatives, though stable in dichloromethane solution, exploded violently when heated as solids [1]. Several diazo-triazoles, -pyrazoles and -imidazoles were found to be explosively unstable in varying degrees [2].

Individually indexed compounds are:
5-Amino-3-phenyl-1,2,4-triazole, : Nitrous acid, 2947
5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2827
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1341
4-Diazo-1,2,3-triazole, 0674
2-Diazo-2H-imidazole, 1079
3-Diazo-3*H*-1,2,4-triazole, 0673
3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2904
3-Diazo-5-phenyl-3*H*-pyrazole, 3112
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1847

DIAZO COMPOUNDS CN_2

In this group of reactive and unstable compounds, the common structural feature is an N=N unit double-bonded to a carbon atom. Individually indexed compounds are:
1-Benzoyl-1-phenyldiazomethane, 3631
1,6-Bis(4-chlorophenyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3737
* Bis(dimethylarsinyldiazomethyl)mercury, 2461
Bis(ethoxycarbonyldiazomethyl)mercury, 2973
2-Buten-1-yl diazoacetate, 2370
tert-Butyl 2-diazoacetoacetate, 3004
tert-Butyl diazoacetate, 2417
5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2827
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1341
Cyanodiazoacetyl azide, 1342
4-Diazo-1,2,3-triazole, 0674
2-Diazo-2H-imidazole, 1079
3-Diazo-3*H*-1,2,4-triazole, 0673
4-Diazo-5-phenyl-1,2,3-triazole, 2905
3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2904
3-Diazo-5-phenyl-3*H*-pyrazole, 3112
Diazoacetaldehyde, 0706
Diazoacetonitrile, 0671
Diazoacetyl azide, 0675
2-Diazocyclohexanone, 2368
Diazocyclopentadiene, 1826

1-Diazoindene, 3110
Diazomalonic acid, 1078
Diazomalononitrile, 1340
Diazomethane, 0405
5-(Diazomethylazo)tetrazole, 0715
Diazomethyldimethylarsine, 1236
3-Diazopropene, 1132
α-Diazo-γ-thiobutyrolactone, 1430
Di-*tert*-butyl diazomalonate, 3405
Dicyclopropyldiazomethane, 2820
Dideuterodiazomethane, 0335
Diethyl diazomalonate, 2824
Dinitrodiazomethane, 0542
1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3738
Disilver diazomethanide, 0305
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1847
Ethyl diazoacetate, 1499
Lithium diazomethanide, 0378
3-Methoxy-2-nitrobenzoyldiazomethane, 3118
Methyl diazoacetate, 1135
2-Nitrophenylsulfonyldiazomethane, 2696
Phenyldiazomethane, 2721
Poly(diazomethylenemercury), 0519
Sodium diazomethanide, 0382
Tetrachlorodiazocyclopentadiene, 1801
2,2,2-Trifluorodiazoethane, 0660
See DIAZOMETHANE SALTS, α-DIAZO-β-OXOSULFONES

DIAZOETHERS

See ARENEDIAZOATES

DIAZOMETHANE SALTS **$Met_2C{=}N{=}N$**

Bertrand, G. *et al., Angew. (Int.)*, 1994, **33**(5), 534@

The disilver, dilithium and ‘dimercury’ salts of this anion [128234-64-0] are too explosive for safe handling. The bis(trimethylstannyl) derivative is a safer substitute.

See DIAZO COMPOUNDS

DIAZONIUM CARBOXYLATES **$N_2^+ArCO_2^-$**

Several of these internal diazonium salts, prepared by diazotisation of anthranilic acids, are explosive in the solid state, or react violently with various materials. Individually indexed compounds (including analogous sulfonates) are:
Benzenediazonium-2-carboxylate, 2655
* Benzenediazonium-2-sulfonate, 2185
Benzenediazonium-3 or 4-carboxylate, 2656

* Benzenediazonium-4-sulfonate, 2186
* 2-Carboxy-3,6-dimethylbenzenediazonium chloride, 3132
* 1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3386
4,6-Dimethylbenzenediazonium-2-carboxylate, 3123
3,5-Dimethylbenzenediazonium-2-carboxylate, 3122
* 2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate, 3234
4-Hydroxybenzenediazonium-3-carboxylate, 2659
4-Iodobenzenediazonium-2-carboxylate, 2635
See other DIAZONIUM SALTS

DIAZONIUM PERCHLORATES $ArN_2^+ ClO_4^-$

1. Hofmann, K. A. *et al., Ber.*, 1906, **39**, 3146; 1910, **43**, 2624
2. Vorländer, D., *Ber.*, 1906, **39**, 2713—2715
3. Burton, H. *et al., Analyst*, 1955, **80**, 4

The diazonium perchlorates are extremely explosive, shock-sensitive materials when dry, some even when damp [1,2]. The salt derived from diazotised *p*-phenylendiamine was considered to be more explosive than any other substance known in 1910 [3].
Individually indexed compounds are:
4-Aminobenzenediazonium perchlorate, 2297
Benzene-1,4-bis(diazonium perchlorate), 2153
Benzenediazonium perchlorate, 2225
4,4′-Biphenylenebis(diazonium) perchlorate, 3451
1(2′-Diazoniophenyl)2-methyl-4,6-diphenylpyridinium diperchlorate, 3841
3-Nitrobenzenediazonium perchlorate, 2148
1- or 2-Naphthalenediazonium perchlorate, 3240
1(2′-, 3′-, or 4′-Diazoniophenyl)-2,4,6-triphenylpyridinium diperchlorate, 3864
2-Toluenediazonium perchlorate, 2736
See other DIAZONIUM SALTS

DIAZONIUM SALTS ArN_2^+

1. Houben-Weyl, 1965, Vol. 10.3, 32—38
2. Doyle, W. H., *Loss Prev.*, 1969, **3**, 14
3. Anon, *Sichere Chemiearbeit*, 1993, **45**(1), 8
4. Fogel'zang, A. E. *et al., Chem. Abs.*, 1974, **81**, 155338
5. Bartsch, R. A. *et al., J. Amer. Chem. Soc.*, 1976, **98**, 6753—6754
6. Storey, P. D., *Runaway Reactions*, 1981, Paper 3/P, 1—9
7. Mustacchi, H. *et al.*, Ger. Offen. DE 3 202 208, 1982
8. Grewer, Th. *et al., Thermochim. Acta*, 1993, **225**(2), 201

A few diazonium salts are unstable in solution, and many are in the solid state. Of these, the azides, chromates, nitrates, perchlorates (outstandingly), picrates, sulfides, triiodides and xanthates are noted as being explosive, and sensitive to friction, shock, heat and radiation. In view of their technical importance, diazonium salts are often isolated as their zinc chloride (or other) double salts, and although these are considerably more stable, some incidents involving explosive decomposition have been recorded.

During bottom discharge of an undefined diazonium chloride preparation, operation of a valve initiated explosion of the friction-sensitive chloride which had separated from solution. The latter did not occur with the corresponding sulfate [2]. Some of a group of industrial diazotisation vessels were closed down, improving gas extraction from those still operated. The ventline later blocked on one vessel and, when attempts were made to open it, disassembled itself explosively. Thick deposits of crystalline diazonium salts were found elsewhere in the system, although only slime had been seen previously. It appears that the improved extraction sucked amines and nitrous gases from the vessels, to complete their reaction in the vent line [3]. The combustive and explosive behaviour of solid diazonium salts at various pressures was studied, including benzenediazonium chloride and nitrate, and *m*- and *p*-nitrobenzenediazonium chlorides [4]. Complexation of diazonium anions with crown ethers reduces or suppresses thermal decomposition of the anion, and may prove useful to stabilise shock-sensitive species [5]. The thermal explosion properties of a series of 10 dimethylamino- or morpholino-substituted benzenediazonium tetrafluoroborates or tetrafluorozincates were studied using DSC, to provide data to assist in practical assessment of stability, particularly towards impact [6]. Diazonium 5-sulfoisophthalate salts are more thermally stable and less flammable than the corresponding tetrafluoroborate and tetrachlorozincate salts [7]. A procedure is given for testing impact sensitivity of diazonium salts by a drop-weight procedure. It is applicable to impure materials of commercial practice. Nitrobenzenediazonium derivatives were found especially sensitive: of critical impact energy 1-2 J [8]. Separately treated groups and individually indexed compounds are:

5-Amino-3-phenyl-1,2,4-triazole, : Nitrous acid, 2947
Benzenediazonium chloride, 2223
Benzenediazonium iodide, 2243
Benzenediazonium nitrate, 2268
Benzenediazonium tetrachlorozincate, 3469
Benzenediazonium tribromide, 2220
* Benzenediazonium-2-sulfonate, 2185
* Benzenediazonium-4-sulfonate, 2186
* 1,10-Bis(diazonio)decaboran(8)ate, 0197
4-Chloro-2-methylbenzenediazonium salts, 2715
5-Chlorotoluene-2-diazonium tetrachlorozincate, 3637
2-Diazonio-4,5-dicyanoimidazolide, 2044
1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3386
3-Diazoniopyrazolide-4-carboxamide, 1418
5-Diazoniotetrazolide, 0545
2-Naphthalenediazonium trichloromercurate, 3242
4-Nitrobenzenediazonium azide, 2202
3-Nitrobenzenediazonium chloride, 2144
4-Nitrobenzenediazonium nitrate, 2198
2- or 3-Toluenediazonium iodide, 2747
* Potassium 1-phenylethanediazoate, 2959
Tetrazole-5-diazonium chloride, 0369
2-Toluenediazonium bromide, 2732

3-Toluenediazonium salts, 2770
2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene, : Hydrochloric acid, 3529
1,2,4-Triazole-3-diazonium nitrate, 0676
3,4,5-Triiodobenzenediazonium nitrate, 2077

ARENEDIAZONIUM OXIDES
DIAZONIUM CARBOXYLATES
DIAZONIUM PERCHLORATES
DIAZONIUM SULFATES
DIAZONIUM SULFIDES AND DERIVATIVES
DIAZONIUM TETRAHALOBORATES
DIAZONIUM TRIIODIDES
See also TETRAZOLES

DIAZONIUM SULFATES $(ArN_2^+)_2\ SO_4^{2-}$, $ArN_2^+\ HSO_4^-$

1. Bersier, P. *et al., Chem. Ing. Tech.*, 1971, **43**(24), 1311—1315
2. Partington, S. *et al., Trans. Inst. Chem. Eng.*, 2002, 80(B), 33
3. Editor's comments
4. Partington S. *et al., Inst. Chem. Symposium Ser.*, 2001, 148(**Hazards XVI**), 81

During investigation after the violent explosion of a 6-chloro-2,4-dinitrobenzenediazonium sulfate preparation made in nitrosylsulfuric acid, it was found that above certain minimum concentrations some diazonium sulfates prepared in sulfuric acid media could be brought to explosive decomposition by local application of thermal shock. Classed as dangerous were the diazonium derivatives of 6-chloro-2,4-dinitroaniline (at 1.26 mmol/g, very dangerous at 1.98 mmol/g); 6-bromo-2,4-dinitroaniline (very dangerous at 1.76 mmol/g); 2,4-dinitroaniline (2.0 mmol/g). Classed as suspect were the diazonium derivatives above at lower concentrations, and those of 2-chloro-5-trifluoromethylaniline (at 1.84 mmol/g); 2,6-dichloro-4-nitroaniline (0.80 mmol/g); 2-methanesulfonyl-4-nitroaniline (0.80 mmol/g); 2-cyano-4-nitroaniline (1.04 mmol/g). A further 11 derivatives were not found to be unstable. Details of several stability testing methods are given [1]. As part of a phenol synthesis, an arylamine dissolved in sulfuric acid was diazotised at 20—40°C by addition of nitrosyl sulfuric acid, and the diazonium salt decomposed in a second reactor to give the phenol. After poor temperature control, when overcooling would have allowed accumulation of unreacted nitrosyl sulfuric, the 123rd batch overheated and then blew the diazotisation reactor apart. Calorimetric investigation showed a two stage exothermic decomposition [2,4]. The first stage, starting little above the intended diazotisation temperature, presumably corresponds to phenol formation, itself usually mildly exothermic as well as gas evolving and best not done as a batch reaction. The more vigorous second stage would be something else, perhaps to be understood if the substrate were stated [3].

Individually indexed compounds are:
Benzenediazonium hydrogen sulfate, 2311
6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate, 2090
6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2095
2-Chloro-4,6-dinitroaniline, : Nitrosylsulfuric acid, 2146

2-Chloro-5-trifluoromethylbenzenediazonium hydrogen sulfate, 2643
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2664
2,6-Dichloro-4-nitrobenzenediazonium hydrogen sulfate, 2099
2,4-Dinitrobenzenediazonium hydrogen sulfate, 2199
2-Methanesulfonyl-4-nitrobenzenediazonium hydrogen sulfate, 2780
See THERMAL STABILITY OF REACTION MIXTURES
See other DIAZONIUM SALTS

DIAZONIUM SULFIDES AND DERIVATIVES **ArN_2S—**

1. Graebe, C. *et al., Ber.*, 1882, **15**, 1683
2. Bamberger, E. *et al., Ber.*, 1896, **29**, 272
3. Nawiasky, P. *et al., Chem. Eng. News*, 1945, **23**, 1247
4. Hodgson, H. H., *Chem. & Ind.*, 1945, 362
5. Tomlinson, W. R., *Chem. Eng. News*, 1957, **29**, 5473
6. Hollingshead, R. G. W. *et al., Chem. & Ind.*, 1953, 1179
7. Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 278
8. Parham, W. E. *et al., Org. Synth.*, 1967, **47**, 107
9. Anon., *BCISC Quart. Safety Summ.*, 1969, **40**, 17
10. Zemlyanskii, N. I. *et al., Chem. Abs.*, 1971, **74**, 53204
11. Spencer, H., *Chem. Brit.*, 1977, **13**, 240—241
12. Petullo, G. *et al., Tetrahedron Lett.*, 1985, **24**, 6365—6368
13. Barbero, M. *et al., J. Org. Chem.*, 2000, **65**(18), 5600
14. Editor's comment

There is a long history of the preparation of explosive solids or oils from interaction of diazonium salts with solutions of various sulfides and related derivatives. An early German worker making arene thiols reported that "in a succesful synthesis the flask held together." Such products have arisen from benzene- and toluene-diazonium salts with hydrogen, ammonium, or sodium sulfides [1,5]; 2- or 3-chlorobenzene-, 4-chloro-2-methylbenzene-, 2- or 4-nitrobenzene- or 1- or 2-naphthalene-diazonium solutions with hydrogen sulfide, sodium hydrogen sulfide or sodium mono-, di- or poly-sulfides [1]—[4,7]. 4-Bromobenzenediazonium solutions gave with hydrogen sulfide at —5°C a product which exploded under water at 0°C [2], and every addition of a drop of 3-chlorobenzenediazonium solution to sodium disulfide solution at 0°C caused a violent explosion [4]. In general, these compounds appear to be bis(arene-diazo) sulfides or the hydrogen sulfides, since some of the corresponding disulfides are considerably more stable [2].

Interaction of 2-, 3- or 4-chlorobenzenediazonium salts with *O*-alkyldithiocarbonate ('xanthate') solutions [8] or thiophenoxide solutions [9] produces explosive products, possibly arenediazo aryl sulfides. The intermediate diazonium xanthate produced during the preparation of *m*-thiocresol can be dangerously explosive under the wrong conditions [8], while the reaction of 3-nitrobenzenediazonium chloride with xanthate solution at 70—75°C proceeds with near-explosive evolution of nitrogen [4]. The product of interaction of 2-chlorobenzenediazonium chloride and sodium 2-chlorothiophenoxide exploded violently on heating to 100°C, and the oil precipitated from interaction of potassium thiophenoxide with 3-chlorobenzenediazonium chloride exploded during mixing of the solutions [9].

Interaction of substituted arenediazonium salts with potassium *O,O*-diphenylphosphorodithioates gave a series of solid diazonium salts which decomposed explosively when heated dry [10]. The unique failure of diazotised anthranilic acid solutions to produce any explosive sulfide derivatives under a variety of conditions has been investigated and discussed [6]. Preparation of diaryl sulfides from interaction of diazonium and thiophenoxide salts led to violent explosions, attributed to presence of some arenediazo sulfide during subsequent distillation of the diaryl sulfides. Precautions are detailed [11]. A safe method of preparation of diaryl sulfides from diazonium tetrafluoroborates and sodium benzenethiolate in DMF is now available [12]. A more widely applicable method is reaction of dried diazonium o-benzenedisulfonimides with sulfur nucleophiles in methanol solution, caution is still advised [13]. A generally safe sulfur nucleophile is thiourea, giving thiouronium salts which are readily hydrolysed to the thiol, which can be oxidised to the disulphide. Since mishap is associated with separation of an explosive organic phase, an inert organic pick-up solvent, in which decomposition would be more controlled, should lend a measure of safety [14].

See Hydrogen trisulfide: Benzenediazonium chloride
    4-Chloro-2-methylbenzenediazonium salts, 2715
    Hydrogen trisulfide : Benzenediazonium chloride, 4479
    3-Quinolinethiol: preparation from the diazonium salt, 3116
    3-Toluenediazonium salts, : Ammonium sulfide, or Hydrogen sulfide, 2770
    3-Toluenediazonium salts, : Potassium *O*-ethyl dithiocarbonate, 2770

DIAZONIUM TETRAHALOBORATES $ArN_2^+ BX_4^-$

1. Olah., G. A. *et al., J. Org. Chem.*, 1961, **26**, 2053
2. Doak, G. O. *et al., Chem. Eng. News*, 1967, **45**(53), 8
3. Fletcher, T. L., *Chem. & Ind.*, 1972, 370
4. Pavlath, A. E. *et al., Aromatic Fluorine Compounds*, 15, New York, Reinhold, 1962
5. Coates, C. F. *et al., Runaway Reactions*, 1981, Paper 4/Y, 1—2

Solid diazonium tetrachloroborates decompose very vigorously, sometimes explosively, on heating in absence of solvent. Dry *o*-nitrobenzenediazonium tetrachloroborate is liable to explode spontaneously during storage at ambient temperature [1]. Hazards involved in drying diazonium tetrafluoroborates have been discussed. The decomposition temperature of any new salt should be checked first on a small sample, and only if it is above 100°C should the bulk be dried and stored. Salts which show signs of decomposition at or below ambient temperature must be kept moist and used immediately [2]. The need to use an inert solvent in any deliberate thermal decomposition is stressed [3], and attention is drawn to an erroneous reference to the use of tetrahydrofuran, which could be hazardous. The presence of nitro substituent groups may greatly increase the decomposition temperature, so that decomposition may become violent or even explosive [4]. The Schiemann thermal decomposition of a tetrafluoroborate salt, previously done repeatedly without incident, became violent on one occasion, causing vessel pressurisation from evolved gas. The presence of impurities had transformed the normally smooth decomposition at 95° to a violent reaction at 84°C [5].

Individually indexed compounds are:
2-Azidomethylbenzenediazonium tetrafluoroborate, 2704
Benzenediazonium tetrafluoroborate, 2216
2-Chloro-3-pyridinediazonium tetrafluoroborate, 1810
5-(4-Diazoniobenzenesulfonamido)thiazole tetrafluoroborate, 3113
5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3670
2-Nitrobenzenediazonium tetrachloroborate, 2121
3-Pyridinediazonium tetrafluoroborate, 1820
See other CATALYTIC IMPURITY INCIDENTS, GAS EVOLUTION INCIDENTS

DIAZONIUM TRIIODIDES $ArN_2^+ I_3^-$

Carey, J. G. *et al., Chem. & Ind.*, 1960, 7
The products produced by interaction of diazonium salts and iodides are unstable and liable to be explosive in the solid state. They are usually the triiodides, but mono-iodides have been isolated under specific conditions from diazotised aniline and *o*-toluidine. Products prepared from diazotised *o*-, *m*- or *p*-nitroanilines, *m*-chloro-, -methoxy-, or -methyl-aniline are too unstable to isolate, decomposing below 0°C.

Individually indexed compounds are:
Benzenediazonium iodide, 2243
Benzenediazonium triiodide, 2247
4-Chlorobenzenediazonium triiodide, 2130
2,4-Dimethylbenzenediazonium triiodide, 2958
2- or 4-Methoxybenzenediazonium triiodide, 2753
4-Toluenediazonium triiodide, 2752
See other DIAZONIUM SALTS, IODINE COMPOUNDS

α-DIAZO-β-OXOSULFONES $RSO_2CN_2CO.R'$

Manteiro, H. J., *Synth. Comm.*, 1987, **17**(8), 983—989
The title compounds were prepared safely by a diazo-transfer reaction onto β-oxosulfones by treatment with 1-ethyl-2-chloropyridinium tetrafluoroborate and sodium azide in presence of sodium acetate.
See DIAZO COMPOUNDS ABOVE

DIAZOTISATION $ArNH_2 \rightarrow ArN_2^+$

1. Houben-Weyl, 1965, Vol. 10.3, 1—112
2. Schierwater, F.-W., *Sichere Chemiearb.*, 1986, **38**(2), 18

In the extensive review of diazotisation, frequent reference is made to the need for close temperature control during processing operations, and to the explosive nature of isolated diazonium salts [1]. Inclusion of methanol in the reaction mixture used to diazotise 2-toluidine, and use of sulfuric acid rather than acetic acid in the ensuing coupling reaction with 2-toluidine to give 2-aminoazotoluene led to formation of a high concentration of methyl nitrite. No explosion occurred, but a fatality resulted from inhaling the fumes escaping from the open port of the reaction vessel [2].

Many examples are covered in the group entries:
ARENEDIAZONIUM OXIDES
DIAZONIUM CARBOXYLATES
DIAZONIUM PERCHLORATES
DIAZONIUM SULFATES
DIAZONIUM SULFIDES AND DERIVATIVES
DIAZONIUM TETRAHALOBORATES
DIAZONIUM TRIIODIDES
See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

I,I-DI(BENZOYLPEROXY)ARYLIODINES $(XC_6H_4CO.OO)_2IC_6HY$

Plesnicar, B. *et al., Angew Chem. (Intern. Ed.)*, 1970, **9**, 707

Compounds of the general structure above, with X = *m*-chloro or *p*-nitro, and Y = H, *p*-chloro or *o*-methoxy, are extremely powerful oxidants, unstable when dry, and will explode during manipulation at ambient temperature (particularly with metal spatulae), or on heating to 80—120°C. The group exceeds the oxidising power of organic peroxyacids. The individual compounds are:
I,I-Bis(3-chlorobenzoylperoxy)-4-chlorophenyliodine, 3787
I,I-Bis(3-chlorobenzoylperoxy)phenyliodine, 3788
I,I-Bis(4-nitrobenzoylperoxy)-2-methoxyphenyliodine, 3813
I,I-Bis(4-nitrobenzoylperoxy)-4-chlorophenyliodine, 3783
I,I-Bis(4-nitrobenzoylperoxy)phenyliodine, 3789
[*I,I*Bis(trifluoroacetoxy)iodo]benzene, 3233
See other DIACYL PEROXIDES, IODINE COMPOUNDS, OXIDANTS

DICHROMATE SALTS OF NITROGENOUS BASES $(N^+)_2Cr_2O_7{}^{2-}$

1. Gibson, G. M., *Chem. & Ind.*, 1966, 553

The dichromates of 1-phenylbiguanide, its *p*-chloro, *p*-methyl and 1-naphthyl analogues all decompose violently at around 130°C.

Individually indexed compounds are:
Ammonium dichromate, 4240
1-(4-Chlorophenyl)biguanidinium hydrogen dichromate, 3000
Dianilinium dichromate, 3531
Dipyridinium dichromate, 3298
Guanidinium dichromate, 0967
1-Phenylbiguanidinium hydrogen dichromate, 3014
4-Tolylbiguanidium hydrogen dichromate, 3176
See other OXOSALTS OF NITROGENOUS BASES

[14] DIENE-N_4 COMPLEXES

1. Goedken, V. L. *et al., J. Amer. Chem. Soc.*, 1972, **94**, 3397
2. Tait, A. M. *et al., Inorg. Synth.*, 1978, **18**, 2—36
3. Peng, S. M. *et al., Inorg. Chem.*, 1978, **17**, 821

The macroheterocylic ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene (abbreviated to [14] diene-N_4) forms cationic complexes with iron(II or III), also containing acetonitrile, imidazole, phenanthroline or halogen ligands. When the anion is perchlorate, the products are explosive, sensitive to heat and impact; some appear to decompose on storage (1 week) and become sensitive to slight disturbance [1]. Details are given for avoiding the use of perchloric acid and/or perchlorate salts in this and structurally related series [2]. Some of the compounds containing perchlorate anions must be regarded as extremely hazardous and potentially explosive. Prepare only minimal amounts, and long term storage above 1 month is not recommended [3]. Individually indexed compounds are:

Acetonitrileimidazole-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3822
Bromo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3716
* *trans*-Bromoazido(meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) perchlorate, 3553
Chloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3718
Copper(II) perchlorate: *N*-(2-Pyridyl)acylacetamides, 4051
Copper(II) perchlorate: Polyfunctional amines, 4051
Diacetonitrile-5,5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3807
Dichloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(III) perchlorate, 3719
5,5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraaza-4,11,-cyclotetradecadiene-1,10-phenanthrolineiron(II) perchlorate, 3863
Hydroxobis[5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] triperchlorate, 3875
Iodo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3717
Oxybis[aqua-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] tetraperchlorate, 3876
See POLYAZACAGED METAL PERCHLORATES
See other AMMINEMETAL OXOSALTS

DIENES C=C=C, C=C—C=C

The 1,2 and 1,3-dienes (vicinal and conjugated, respectively) are more reactive than the separated dienes.

Individually indexed compounds are:
7-Azidobicyclo[2.2.1]hepta-2,5-diene, 2773
* 1,4-Benzoquinone diimine, 2303

* 1,4-Benzoquinone monoimine, 2253
† Bicyclo[2.2.1]hepta-2,5-diene, 2785
† 1,2-Butadiene, 1475
† 1,3-Butadiene, 1476
† 2-Chloro-1,3-butadiene, 1447
* *N*-Chlorocinnamaldimine, 3120
† 1,3,5-Cycloheptatriene, 2786
† 1,3-Cyclohexadiene, 2354
† 1,4-Cyclohexadiene, 2355
† 1,3,5,7-Cyclooctatetraene, 2937
* 1,3,5-Cyclooctatriene, 2961
† Cyclopentadiene, 1851
2,3-Diazido-1,3-butadiene, 1433
† Dicyclopentadiene, 3293
2,3-Dimethyl-1,3-butadiene, 2401
* 3,7-Dimethyl-2,6-octadienal, 3340
4,5-Hexadien-2-yn-1-ol, 2321
† 1,5-Hexadien-3-yne, 2284
1,3-Hexadien-5-yne, 2283
† *trans*-2-*trans*-4-Hexadiene, 2407
† *cis*-2-*trans*-4-Hexadiene, 2406
† 1,5-Hexadiene, 2405
† 1,4-Hexadiene, 2404
† 1,3-Hexadiene, 2403
1-Iodohexa-2,4-diene, 2387
Limonene, 3331
1,5-*p*-Menthadiene, 3332
* Methoxy-1,3,5,7-cyclooctatetraene, 3143
† 3-Methyl-1,2-butadiene, 1886
† 2-Methyl-1,3-butadiene, 1887
† 4-Methyl-1,3-pentadiene, 2411
† 2-Methyl-1,3-pentadiene, 2410
Methylcyclopentadiene, 2356
* 2-Nitrosophenol (1,2-Benzoquinone monoxime), 2256
† 1,7-Octadiene, 3016
* 1,3,7-Octatrien-5-yne, 2938
† 1,2-Pentadiene, 1889
† 1,3-Pentadiene, 1890
† 1,4-Pentadiene, 1891
Perfluorobutadiene, 1360
* Poly(1-pentafluorothio-1,2-butadiyne), 1375
* Poly(acetylene), 0683
* *cis*-Poly(butadiene), 1480
† Propadiene (Allene), 1121
1,1,2,3-Tetrachloro-1,3-butadiene, 1385
* 1,1,4,4-Tetrachlorobutatriene, 1356

Tetracyclo[4.3.0^{3,5}.0^{4,6}]nona-1,7-diene, 3119

∗ 1,1,4,4-Tetrafluorobutatriene, 1359

See Oxides of Nitrogen

Nitrogen oxide: Dienes, Oxygen

See other PEROXIDISABLE COMPOUNDS

DIESEL ENGINES

1. Sheldrick, G., *Chem. & Ind.*, 1969, 1823
2. Young, J. A., *CHAS Notes*, 1991, **IX**(5), 2
3. Bond, 1991, 50

In the vicinity of hydrocarbon or solvent spillages, these engines may take in enough fuel with their air supply. In consequence, they cannot be stopped by cutting the supply of fuel from the tank, perpetuating combustion which may not stay internal [1,3]. Precautions against flashback are detailed. Problems can also arise if the engine is driving the pump which is spilling the volatile material [2]. Similar problems could, in principle, occur with gas turbines.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

1. Gygax, R. *et al., Therm. Anal.*, 1980, **1**, 541—548
2. Brogli, F. *et al., Therm. Anal.*, 1980, **1**, 549—554
3. Cardillo, P. *et al., Runaway Reactions*, 1981, Paper 3/N, 1—9
4. Dale, D. J., *Org. Proc. Res. & Dev.*, 2002, **6**(6), 933

The scope and limitations of the use of DSC as a means of investigating the reaction dynamics of potentially hazardous chemical reactions is discussed. For existing processes, examination of production samples taken at various stages of the overall process sequence can identify the stage at which maximum heat production is occurring, as the most critical phase for control requirements. The existence of an induction period can also be established, and use of the instrument in its more sensitive isothermal mode can yield information on consecutive reactions and catalytic effects [1]. The place of DSC in a screening programme to estimate hazards in proposed chemical processes is discussed in detail. The use of pressure-tight encapsulated samples permits rapid assessment of heats of reaction and/or decomposition and kinetic behaviour under likely process conditions. Selected case studies are included [2]. The part played by DSC in the investigation of the Seveso incident has been discussed [3]. A critique of DSC for screening reactions suggests a somewhat larger scale alternative, also capable of showing pressure generation [4].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

DIFFERENTIAL THERMAL ANALYSIS (DTA)

1. Corignan, Y. P. *et al., J. Org. Chem.*, 1967, **32**, 285
2. Prugh, R. W., *Chem. Eng. Progr.*, 1967, **63**(11), 53
3. Krien, G., *Diff. Therm. Anal.*, 1972, **2**, 353—377
4. Duswalt, A. A., *Thermochim. Acta*, 1974, **8**(1—2), 57—58
5. Berthold, W. *et al., Chem. Ing. Tech.*, 1975, **47**, 368—373

6. Giger, G. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, C14—23, Rugby, IChE, 1983
7. Cassel, R. B., *Perkin-Elmer Therm. Anal. Appl. Study*, 1979, **28**, 1—6

Thermal stabilities of 40 explosive or potentially explosive *N*-nitroamines, aminium nitrates and guanidine derivatives were studied in relation to structure; 14 of the compounds decomposed violently when the exotherm occurred [1]. The value of the DTA technique in assessing hazards of compounds or reaction mixtures is discussed [2]. DTA data on thermally unstable materials (peroxides) as well as explosives was reviewed [3]. The use of various DTA methods for defining processing, storage, and safe reaction conditions has been investigated, and experiences and conclusions were discussed [4]. Use of DTA and DSC methods for predictions in preventing thermal explosions by assessing the stable range of operations in large storage containers are discussed [5,6], with experimental details and exemplification using nonyl nitrate [5] and an unidentified compound [6]. Details of a new ASTM standard method E537-76 for determination of potential explosive hazard by studying the kinetics of thermal decomposition by DTA were discussed [7].

Some of the individual compounds examined are:
Ammonium 1,2-ethylenebis(nitramide), 0968
3-Azoniabicyclo[3.2.2]nonane nitrate, 3043
N,N′-Diacetyl-*N,N′*-dinitro-1,2-diaminoethane, 2420
Diaminoguanidinium nitrate, 0511
1,3-Dinitro-2-imidazolidinone, 1139
N,N′-Dinitro-*N*-methyl-1,2-diaminoethane, 1272
1,3,6,8-Tetraazoniatricyclo[6.2.1.1^{3,6}]dodecane tetranitrate, 3086
1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine, 1600
Triaminoguanidinium nitrate, 0514
Triaminoguanidinium perchlorate, 0512
See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

DIFLUOROAMINOALKANOLS $F_2NC(RR')OH$

Fokin, A. V. *et al., Chem. Abs.*, 1970, **72**, 78340

A series of 1-difluoroaminoalkanols prepared from difluoramine and an aldehyde or ketone, together with their acetates or bis(ethers), were all shock- and friction-sensitive explosives.

See other DIFLUOROAMINO COMPOUNDS

DIFLUOROAMINO COMPOUNDS RNF_2

1. Freeman, J. P., *Adv. Fluorine Chem.*, 1970, **6**, 321, 323
2. Dalinger, I. L. *et al., Mendeleev Comm.* 1996, (1), 13

All organic compounds containing one or more difluoroamino groups should be treated as explosive oxidants and excluded from contact with strong reducing agents. If the ratio of NF_2 to CH_2 groups is above 1:5, the compound will be impact-sensitive. Direct combustion for elemental analysis will be unsafe, but polarography is applicable. Many difluoroamines, often also having nitro-groups, have been studied as explosives in their own right, or mixed with active metals [1]. A synthesis of N-difluoroaminoazoles, which are heterocyclic 1,1-difluorohydrazines, has been described. They are shock sensitive [2].

Individually indexed compounds are:
1,1-Bis(difluoroamino)-2,2-difluoro-2-nitroethyl methyl ether, 1101
4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene, 1861
Bis(difluoroamino)difluoromethane, 0361
1,2-Bis(difluoroamino)ethanol, 0798
1,2-Bis(difluoroamino)ethyl vinyl ether, 1492
1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0799
2-Cyano-1,2,3-tris(difluoroamino)propane, 1428
Di-1,2-bis(difluoroaminoethyl) ether, 1493
3-Difluoroamino-1,2,3-trifluorodiaziridine, 0357
(Difluoroamino)difluoroacetonitrile, 0626
N,N-Difluorotrifluoromethylamine, 0356
1,1-Difluorourea, 0397
* Pentafluoroguanidine, 0358
C,N-Perfluoro-*N*-aminomethyltriaminomethane, 0645
Perfluoro-*N*-cyanodiaminomethane, 0633
† Tetrafluorohydrazine, 4339
Tetrafluorourea, 0351
Tris(difluoroamino)fluoromethane, 0363
See BIS(DIFLUOROAMINO)ALKYL NITRATES
See other N-HALOGEN COMPOUNDS

DIFLUOROAMINOPOLYNITROARYL COMPOUNDS

Lerom, M. W. *et al., J. Chem. Eng. Data*, 1974, **19**, 389—392
Several difluoroaminopolynitro derivatives of stilbene, biphenyl, terphenyl and their precursors are explosives, sensitive to initiation by impact, shock, friction or rapid heating.
See other DIFLUOROAMINO COMPOUNDS

DIFLUOROPERCHLORYL SALTS $F_2ClO_2^+ Z^-$

Organic materials, or Water
Christe, K. O. *et al., Inorg. Chem.*, 1973, **12**, 1358
Difluoroperchloryl tetrafluoroborate, hexafluoroarsenate or hexafluoroplatinate all react violently with organic materials or water. Individual salts are:
Difluoroperchloryl hexafluoroarsenate, 0093
Difluoroperchloryl hexafluoroplatinate, 3985
Difluoroperchloryl tetrafluoroborate, 0123
See Chlorine dioxygen trifluoride

DIGESTION

Geological and biological sample preparation for subsequent analysis often involves digestion in highly oxidant media such as nitric or perchloric acid. This is a frequent cause of incidents, which will be found under the entries for digestion reagents. It is also necessary to consider that the apparatus, or parts of it such as mounts and sealing rings, may be constructed of materials themselves digestible.

DIISOCYANIDE LIGANDS $:C{=}N{-}C[CH_2]_nC{-}N{=}C:$

1. Yaneff, P. V. *et al., J. Organomet. Chem.*, 1979, **179**, 111
2. Howell, J. A. *et al., J. Chem. Soc., Dalton Trans.*, 1981, 301

It is preferable to prepare and use various diisocyanide ligands (trimethylene to octamethylenene diisocyanides, 1,4-dimethylenecyclohexane and 1,3-xylylidene diisocyanides) as solvent solutions rather than as isolated materials, because violent explosions have been observed during vacuum distillation of these ligands [1]. Four such ligands were, however, distilled uneventfully [2]. Individually indexed compounds are:

1,3-Bis(isocyanomethyl)benzene, 3251
1,4-Bis(isocyanomethyl)cyclohexane, 3324
1,4-Diisocyanobutane, 2365
1,6-Diisocyanohexane, 3001
1,8-Diisocyanooctane, 3337
1,5-Diisocyanopentane, 2821
1,3-Diisocyanopropane, 1863
1,1,1-Triazidodinitroethane, 0679

See related CYANO COMPOUNDS

1,1-DINITRODIFLUORAMINES $RC(NO_2)_2NF_2$

Fokin, A. V. *et al., Dokl, Akad. Nauk.*, 1996, **346**(3), 358; *Chem. Abs.*, 1996, **125** 167297

A variety of these compounds were prepared (R = CN, $CONH_2$, Me, Ph). Not surprisingly they were explosives very sensitive to shock, friction and heat. They were inclined to distillation during distillation.

See also *N*-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

1,2-DIOLS —C(OH)C(OH)—

Preparative hazard

See Sodium chlorate: Alkenes, Potassium osmate

1,3,4-DIOXAZOLONES

Middleton, W. J., *J. Org. Chem.*, 1983, **48**, 3845—3847

2-Perfluoroalkyl-1,3,4-dioxazolones are a potentially hazardous group of compounds, being capriciously explosive. They are no safer than perfluoroacyl azides as precursors for isothiocyanates.

See other DIOXETANES, N—O COMPOUNDS

DIOXETANES

1. Mumford, C., *Chem. Brit.*, 1975, **11**, 402
2. Kopecky, K. R. *et al., Can. J. Chem.*, 1975, **53**, 1103—1122
3. Livingstone, R., Rodd, (Supplement to 2nd Edn.), IVa, 1984
4. Adam, W. *et al., J. Amer. Chem. Soc.*, 1994, **116**(17), 7581

This group of highly strained cyclic peroxides, though thermodynamically unstable, contains some compounds of sufficient kinetic stability to exist as solids at ambient temperature [1]. Interest in these compounds is increasing, most are very unstable, several have proved explosive when isolated [2,3]. Not only are lower 1,2-dioxetanes dangerously unstable but so, above 0°C, are the precursor 1,2-bromohydroperoxides [4].

See Tetramethyl-1,2-dioxetane

See other CYCLIC PEROXIDES, STRAINED-RING COMPOUNDS

DIOXYGENYL POLYFLUOROSALTS **$O_2^+[MF_n]$ or O_2^+ $[EF_n]$**

1. Bailar, 1973, Vol. 2, 778—779
2. Griffiths, J. E. *et al., Spectrochim. Acta*, 1975, **31A**, 1208

Dioxygenyl hexafluoro-antimonate, -arsenate, -phosphate, -platinate and -stannate, also tetrafluoroborate, all react very violently with water, liberating ozone and oxygen [1]. Irradiation for Raman spectroscopy of a range of the title compounds and their nitrosyl analogues in glass or quartz capillaries caused many of them to decompose explosively. A special rotating sapphire/Teflon cell overcame the problem. Compounds examined were dioxygenyl hexafluoro-arsenate, -bismuthate, -ruthenate, -rhodate, -platinate and -aurate; dioxygenyl undecafluorodi-antimonate, -niobate and -tantalate; and their nitrosyl analogues [2].

See other IRRADIATION DECOMPOSITION INCIDENTS

DIPHENYL BLACK

Anon., *Loss Prev. Bull.*, 1980, (030), 160

A batch of the trisazo dyestuff, after drying at 100—105°C in a circulating air dryer, was left in the unheated dryer overnight. Exothermic decomposition set in after some hours.

See other AZO COMPOUNDS

DIPLUMBANES **R_3PbPbR_3**

Sidgwick, 1950, 595

The higher members of the hexaalkyldiplumbane series may disproportionate explosively during distillation.

See other ALKYLMETALS

1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES

Anderson, J. R. *et al., J. Org. Chem.*, 1975, **40**, 2016

Several substituted title salts, intermediates in the preparation of 1,3-diselenole-2-selenones, exploded on heating, ignition or shock. The tetrafluoroborate salts were

stable, safe intermediates for large-scale application. Individually indexed compounds are:
1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate, 3334
2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate, 3402
1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate, 3168
1-(4-Phenyl-1,3-diselenonylidene)piperidinium perchlorate, 3652
See other OXOSALTS OF NITROGENOUS BASES

DISPOSAL

1. *Hazardous Chemicals: Information and Disposal Guide*, Armour, M. A. *et al.*, Edmonton, University of Alberta, 1984
2. *Handbook of Laboratory Waste Disposal,* Pitt, E. & M. J.,Chichester (UK), Ellis Horwood, 1985.
3. Chivers, G. E., *Disposal of Hazardous Wastes*, Northwood (Mdx.), Science Reviews Ltd., 1983
4. *Hazardous and Toxic Materials: Safe Handling & Disposal*, Fawcett, H. H., New York, Wiley, 1984
5. *The Disposal of Hazardous Waste from Laboratories*, Proceedings of RSC Chemical Information Group meeting, March 1983, London, RSC, 1983
6. Voegelein, J. F., *J. Chem. Educ.*, 1966, **43**, A151—157
7. Teske, J. W., *J. Chem. Educ.*, 1970, **47**, A291—295
8. Allen, R. O., *J. Chem. Educ.*, 1983, **60**(3), A814
9. Cook, J. D., reference 4 above, 116
10. Ghosh, P. K. *et al., Proc. 11th Int. Sympos. Prev. Occup. Risks Chem. Ind.*, 703—719, Heidelberg, ISSA, 1987
11. U.S. Environmental Protection Agency, Case Study EPA 550-F00-001, 2000
12. Li, H. *et al., J. Hazard. Mat.*, 1999, **69**(2), 129

The gap left in the literature on disposal of hazardous laboratory materials by the withdrawal in 1980 of the MCA manual has been filled adequately by new compilations. In addition to providing brief details on general properties, reactive and toxic hazards for each of some 300 laboratory chemicals, detailed directions for disposal of spills, residues or package lots are available. Disposal methods have been laboratory tested for completeness of reaction, safety and practical utility [1]. All aspects of the implications and operation of UK hazardous waste legislation and the derived practical systems are covered in a 100 page survey, which includes a chapter on disposal of wastes from chemical, biological and radiochemical laboratories [2]. The third reference is concerned more with the long-term implications of past and previous large-scale disposal procedures than with the practical detail of laboratory disposal methods [3]. Many aspects of the complex problems and practical solutions related to disposal of laboratory wastes were covered comprehensively in a symposium [4]. Practical solutions to disposal problems adopted by an explosives research laboratory [5], and by two American universities have been described [6,7], the former including details on the use of explosives to rupture corroded and unusable cylinders of compressed or liquefied gases.

Some of the techniques employed need a remote area for safe operations, which may not be available to laboratories in urban locations. In such cases the services of a specialist chemical disposal contractor may be the most practical solution. It is, however, possible to minimise disposal problems by strict control on quantities ordered for stock (resisting bargain bulk offers), and on stockroom procedures. The reasons for the reluctance of many practising chemists to accept the fact that they are, almost invariably, the person best qualified to deal at the point of origin with difficult or dangerous residues were discussed [8]. Problems encountered and their solutions in disposing of inventories after a chlorine leak in a disused chemical factory are discussed. A large spill of liquid chlorine was largely absorbed in sodium hydroxide. Vinyl chloride was pumped out and removed, hydrogen was released slowly to atmosphere and acetylene was flared off [9]. Of late years, incineration is increasingly recommended Given suitable scrubbing of off-gas, this is a good technique for all organics and many inorganics. Many remarkable elaborations on combustion have been described, such as surrounding a small package of combustible material in high explosive, placing in a chamber full of oxygen and detonating the explosive [11]. Other techniques less obviously hazardous but perhaps worse are to be found in texts devoted to disposal, such as reduction with Raney nickel alloy in strong sodium hydroxide. This always gives far more waste than you started with, and much of that waste may be more noxious, while having the hazards of excess hydrogen, caustic spray and pyrophoric nickel to contend with during the destruction. Not all books are gospels.Waste solvents, mixed with reactor tars and other combustibles, are commonly disposed of as fuel for cement kilns (which have considerable ability to entrap inorganic impurities). A fatal explosion resulted from an attempt to dispose of solid, oxidant, laboratory wastes — perchlorates, chlorates and nitrates — as a dispersion in organic wastes intended as fuel. There might have been no mishap had a very low concentration suspension been prepared and kept dispersed. However, solids, perhaps ten kg quantities, were charged to about 800 litres of solvent, in any event below minimum stir volume for the mixing vessel, with the agitation off. No dispersion meant settling and violent local reaction, followed by a fireball, within a minute. Oxidants and fuels should not be mixed without full understanding of any reaction [10].

There are numerous instances in this handbook of laboratory waste bottles, or industrial waste drums, slowly pressurising and then bursting. In the latter case, sometimes the consequences are fatal. It is unwise to seal a freshly filled waste container tightly, ideally they should be left slightly less than air-tight and only sealed immediately before transport for final disposal.

1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE SALTS

Preparative hazard

See Carbon disulfide: Alkali metals

DRUMS (BARRELS)

Several accidents in this book, some fatal, involve bursting forty-five gallon (215 litre, 55 gallon US) steel drums, a standard chemical packaging. These are sometimes attributed to setting off an explosion in the headspace of a bulging drum while attempting to vent it. In fact, a bulging drum can contain quite enough mechanical energy to kill, cut pipelines, etc. A bulging drum will eventually burst unattended, but the last straw, which breaks the worker's neck if he is in the wrong position, may be the slight additional stress of handling. The most damage results when the bottom blows out, this creates what, in military terms, is a spigot mortar, allowing the compressed gas in the headspace to transfer most of its energy to the bulk of the drum. Since the bottom is under more stress, both chemical and physical, than the top, having the weight of the contents as well as the gas pressure to resist, such failure is probable in a symmetric drum. Any worker standing above the drum while trying to vent it may then be struck hard beneath the chin by 15kg of percussive instrument travelling at modest speed — result a broken neck. Do not stand above bulging drums when trying to vent them. The relatively light, if sharp edged, top plate, though accelerated over a very short distance before the gas vents, is still dangerous. Chemists must beware of storing materials which can either generate gas, react with the drum to produce hydrogen, or be catalysed by it to self-heat to boiling.

See STEEL: Apricots

DRYING

1. *High Vacuum Techniques for Chemical Syntheses and Measurements*, Plesch, P. H., Cambridge, Cambridge University Press, 1989, pp. 140, 141
2. *Purification of Laboratory Chemicals*, Perrin, D. D., Armarego, W. L. F. (Eds.), New York, Pergamon, 3rd edn.
3. *Drying: Principles and Practice*, Keey, R. B., Oxford, Pergamon, 1972
4. *Spray Drying Handbook*, Masters, K., Harlow (Essex), Longmans, 5th edn. 1992
5. *Industrial Drying Equipment Selection and Application*, van't Land, New York, Marcel Dekker, 1991

In the strict chemical sense, the term drying refers to removal of water present in solid or fluid materials by treatment with water-reactive chemicals. In a wider (chemical engineering) context, it also refers to use of physical methods to remove any unwanted liquids (or vapours) from solid, liquid or gaseous phases.

The first reference is largely devoted to small scale and intensive drying of solvents and reagents by chemical methods for use in kinetic work. Chemical drying is commonly a source of hazard since the reagents used are, of their nature, often extremely reactive, and not only with water; a discussion of hazards is given [1]. A good example of such an agent is magnesium perchlorate (Anhydrone) which reacts with a variety of chemicals or solvents to form explosive products or adducts. Generally its use should be avoided. The next reference covers various aspects of laboratory scale purification and possibly less rigorous drying of a wider range of materials [2].The remaining references cover chemical engineering aspects of industrial drying operations, with attention to safety aspects [3,4,5].

Drying, usually by physical methods, is one of the most common unit operations in both laboratory or industrial scale process chemistry, and since heating is usually employed to remove volatiles, thermally unstable materials may decompose if overheated. As a light-hearted example, when a faulty oven thermostat led to overheating of mercuric thiocyanate, a monstrous 'Pharaoh's serpent' resulted. Drying moist cadmium propionate in an electric oven led to explosive ignition of the diethyl ketone vapour produced as an unforeseen by-product. Drying 3,5-dinitro-2-toluamide had more serious consequences.

Chemical drying of liquids often involves reaction, with or without heating, of a solid which will react selectively with water. Calcium or lithium aluminium hydrides are often used; evolved hydrogen needs safe venting. For the lithal, careful stirring and temperature control is essential to prevent formation of extremely reactive aluminium, which may react violently with oxygenated or halogenated solvents like dioxan or trichloroethane.

When adsorbents are used to dry gases or liquids, often in a flow system, the adsorbents may need pre-or post-treatment to avoid hazards. Thus, when ethylene was contacted with molecular sieve not previously treated with dilute ethylene, the adsorption exotherm heated the bed to red heat and ruptured the drier. When peroxide-containing ethers are simultaneously dried and purified by chromatography (passage through an alumina column), the peroxides are concentrated on the alumina, which must be treated before disposal.

The drying of solids may involve the removal of volatile solvents. When these are flammable, ignition sources must be excluded to minimise risk of fire or explosion.

Some industrial drying techniques have inherent potential hazards. The conditions prevalent in spray drying, where a solution is sprayed into a hot gas (usually air), are likely to cause electrostatic charge generation, and stringent earthing/bonding precautions are necessary for flammable solvents or combustible solutes such as milk powder. Fluidised-bed driers may show similar problems with dusty organic materials, and gas-inerting is desirable.

There are unusual hazards associated with partial desolvation of crystalline solvated oxosalts, notably perchlorates. This may be because desolvation causes the oxygen balance to approach the zero balance point and maximum energy release potential. A similar effect has also been seen with an hydrated salt.

These and other examples may be found in the entries:
Cadmium propionate, 2412
Calcium acetylide: Methanol, 0582
Diazomethane: Calcium sulfate, 0405
3,5-Dinitrotoluamide, 2936
Lithium tetrahydroaluminate: Dioxane, 0075
Magnesium perchlorate, 4078
Magnesium: Methanol, 4685
Mercury(II) thiocyanate, 0975
Silicon dioxide: Hydrochloric acid, 4833
Sodium azide Heavy metals, 4753
Sodium: Halocarbons (reference 10), 4790

Sulfuric acid: Hydrofluoric acid, 4473
Vinyl acetate: Dessicants, 1527
METAL—HALOCARBON INCIDENTS (references 2, 3)
MILK POWDER
MOLECULAR SIEVE INCIDENTS: Ethylene
ORGANIC POWDER HANDLING
PEROXIDES IN SOLVENTS
SOLVATED OXOSALT INCIDENTS
See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, VACUUM OVENS
See also FLASH POINTS
See other UNIT OPERATIONS AND PROCESSES

DINITROSOMETHANIDES $(ON)_2CH^- Met^+$

Brand, H. *et al., J. Amer. Chem. Soc.*, 2005, **127**(5), 1360
The mono- lithium, sodium, potassium and caesium salts of dinitrosomethane have been characterised. They are highly explosive, heat and shock sensitive.
See also NITROALKANES: Alkali metals

DUST EXPLOSION INCIDENTS

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16. Enright, R. J., *Chem. Abs.*, 1987, **106**, 125260; **110**, 120443h
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Laboratory dust explosion data were presented for 73 chemical compounds, 29 drugs, 27 dyes and 46 pesticides, including ignition temperatures of clouds and layers, minimum ignition energy, explosion-limiting concentrations and pressures, and rates of rise at various dust concentrations. Explosibility indices were computed where possible and variation of explosibility parameters with chemical composition was discussed. General means of minimising dust explosion hazards were reviewed [1]. Of the 17 dusts investigated earlier, the 4 metals examined — aluminium, magnesium, titanium and zirconium — were among the most hazardous. Aluminium and magnesium show the maximum rates of pressure rise and final pressures, magnesium having a low minimum explosive concentration. Ignition of zirconium dust often occurred spontaneously, apparently owing to static electric discharges, and undispersed layers of the dust could be ignited by less than 1 μJ compared with 15 μJ for a dispersed dust. All except aluminium ignite in carbon dioxide atmospheres [2]. A comprehensive account of practical and theoretical aspects of laboratory and plant-scale dust explosions and fires includes appended tabulated data for over 300 dusts of industrial significance [3]. Laboratory dust explosion data for 181 miscellaneous hazardous materials and 88 non-hazardous materials are presented [4]. Papers and symposium discussions on several aspects of the topic were presented [5], together with further data on dust-explosivity of several metallic and non-metallic industrial materials [6]. A comprehensive survey of the whole field has (1991) been published [35], and rapidly gone to a second edition.

A review including fluid mechanical considerations and useful applications among other aspects of dust explosions [7], and a collection of abstracts covering 20 years to 1977 [8] have been published. In a comparative study of laboratory methods available for assessing dust explosibility, the influence of ignition source type and containing vessel size are discussed in detail [9]. Spontaneous combustion and explosion of natural fuel dusts are covered [10], and a new text on the topic is available [11]. The ultimate experiments in dust explosion research in full size 500 m^3 silos using wheat grain, soya meal and maize starch dusts have been described [12]. Explosions of dispersed 200 mesh cellulose dust was inhibited by presence of potassium chloride, lead nitrate and cadmium sulfate, but promoted by barium chloride or potassium nitrate above 1.3% conc. [13]. A new bibliography (163 entries, 1970—84) cites dust generated explosion details in various industrial environments, particularly agricultural, and classifies combustible dusts [14]. An extensive series of papers on many aspects of dust explosions are collected in [36].

The lower explosive limit and minimum explosive concentrations of flax, wool, cotton, jute, hemp and sisal fibres are of the same order of magnitude as those of highly explosive dusts [15]. The explosibility of pyrites dusts with sulfur contents above 20% was evaluated experimentally. Dusts of 30% sulfur content gave explosion pressures of 3 bar at pressure rise rates of 16 bar/sec. Mixtures of 60% pyrites and 40% powdered limestone still showed significant pressure effects, and the proportion of limestone actually needed to suppress explosions was considerably above the values currently accepted by mining industries [16]. Effects of mixtures of particle sizes in combustible dusts upon minimum ignition temperature (T_i^m) and upon presence or absence of explosion were studied. Presence of 30% of fines in a coarse dust lowers T_i^m significantly [17]. Experimental explosions of polyethylene, phenolic resin, dye, and aspirin powders demonstrated the resistance to explosion of an industrial dust collector fitted with automatic explosion relief panels [18]. The validity of suppressing dust explosions in volumes up to 1000 m^3 using a few large suppressors has been established [19], and the efficacy of the system was proven in an experimental spherical vessel 6.3 m in diameter [20]. The maximum explosion pressures for relatively fine and dry peat dusts may be estimated with a fair degree of accuracy from the moisture content, provided that the mean particle size is below 200 μm and that the moisture content is below 35%. For coarser and moister peat dusts, it may only be possible to assess whether it is explosive, and inhomogeneity in peat samples causes further significant problems [21].

In a comprehensive review of dust explosion problems and hazards associated with mechanical handling systems (pneumatic, screw, and belt conveyors, bucket elevators, en masse conveyors) for bulk transfer of a wide variety of solid chemicals and industrial materials, tabulated data for some 400 such materials are presented. The data are given under the headings minimum ignition temperatures, explosible concentrations in air, and ignition energies; and maximum explosion pressures, rates of pressure rise, and oxygen concentrations to prevent ignition. Of these 400 materials, 33 are notable in that the maximum rates of pressure rise observed exceed 680 bar/s (10,000 psi/s). Figures below for these 33 materials are for maximum explosion pressure (bar) and maximum rate of rise (bar/s), respectively, except where noted.

Acetoacet-4-phenetidide, 5.9, 680; atomised aluminium, 5.7, > 1.36 kbar/s; aluminium flake, 8.6, > 1.36 kbar/s; aluminium—cobalt alloy, 6.25, 748; aluminium—magnesium alloy, 5.85, 680; aluminium—nickel alloy, 6.5, 680; aluminium stearate, 5.85, 680; benzoic acid, 6.85, 700; 2,2-bis(4-hydroxyphenyl)propane, 5.5, 803;

calcium silicide, 5.85, 1.36 kbar/s; calcium stearate, 6.6, > 680; cellulose nitrate, > 17.4, > 1.42 kbar/s; 2-chlorobenzylidenemalononitrile, 6.1, > 680; coumarone—indene resin, 6.3, 748.

1,4-Diaminobenzene, 6.4, 748; 2,6-di-*tert*-butyl-4-cresol, 5.4, 884; dimethyl terephthalate, 7.1, 816; 3,3′-dimethoxy-4,4′-diaminobiphenyl, 5.6, 680; 3,5-dinitrotoluamide, 10.4, 680; 1,3-diphenyltriazene, 7.75, > 680; 2,4-hexadienoic acid, 7.2, > 680; hexamethylenetetramine, 6.7, 748; magnesium, 7.9, 884; paraformaldehyde, 9.0, 884; phytosterols, 5.2, > 680; poly(acrylonitrile), 6.0, 748; rosin, 5.7, 816; silicon, 6.4, 884; tetraphosphorus decasulfide, 4.35, > 680; thorium hydride, 5.5, 816; titanium, 5.8, 816; titanium hydride, 8.2, 816; zinc stearate, 5.4, > 680; zirconium, 5.1 bar, 740 bar/s [22]. In the proceedings of the 1986 Pittsburgh conference on dust explosions, many aspects of the occurrence, prevention and protection from the effects of industrial dust explosions involving a wide variety of materials are presented in a series of papers [23].

Lower limits of explosibility of several organic dusts were determined and found to be in general agreement with estimated values [24]. Probabalistic aspects of occurrence of dust explosions were studied experimentally with lycopodium powder in relation to dust and hot surface (or dust) temperature. The probability of explosion increases with dust concentration, then falls off, due to the ballast effect of unburnt dust. Probability also increases continuously with the temperature of the hot surface and/or dust particles. Application of the results to practical plant installations is discussed [25]. The effect of turbulence (which increases degree of dispersion and reduces the rate of settlement) on closed-volume explosions of dust—air mixtures has been studied [26]. In a 2 part publication, test methods and derived parameters, and preventive and protective measures are reviewed in relation to explosions in combustible dusts and in their mixtures [27]. A method has been described to assess the effect on explosion energy of presence of low concentrations of flammable vapours in dust—air mixtures in a 20 l chamber. Significant increases in rate of pressure rise were observed in corn starch—air mixtures with added refuse-derived fuel vapour [28]. The effect of turbulence on explosion parameters of lycopodium dust in a 1.2 l Hartmann bomb has been studied in two parallel series of experiments. One series in the bomb gave relation between dispersing air pressure, dust concentration, ignition delay time and the maximum rate of pressure rise. A second series in a plexiglass version of the bomb (without ignition) showed the relation beteen dispersing air pressure and dust velocity (measured by laser Doppler velocimeter) and settling time. The decay of turbulence in the Hartmann bomb is rapid (below 200 ms), and this time frame coincided closely with the rapid fall off in the rate of pressure rise with ignition delays of 40—180 ms. The correlation depends on dust concentration and dispersing air pressure [29]. The explosive behaviour of mixtures of flax dust and fibres with air has been studied [30]. The influence of air velocity upon ignition and flame propagation in dust—air mixtures under pneumatic tube conveyor conditions has been studied [31]. Minimum quenching distances for control of dusts of cornstarch, aluminium and coal have been determined [32], and flame propagation and transition to detonation has been studied in mixtures of organic dusts with oxygen-enriched air [33]. A survey of dust fires and explosions in UK during 1979—84 revealed that dusts most frequently involved were those of grains and cereals, animal feeds and food products, while wood and metal dusts were often involved. Other dusts involved were sulfur, phosphorus trisulfide, zinc phosphide, carbon and rubber. Losses from dust fires were more common than from dust explosions [34].

Mist explosions are, of course, dust explosions in which the particles happen to be liquid. A study of criteria for these, with especial reference to organic heat transfer fluids, is reported [39]. Other less common types of heterogeneous explosion involving gaseous oxidants are reviewed [37] [40]. These include wick explosions, foam explosions, and surface explosions. Studies aimed at early detection and suppression of dust explosions are reported [38].

Individually indexed incidents include:

Acetoacet-4-phenetidide, 3523
O-Acetylsalicylic acid, 3131
Aluminium, 0048
Aluminium stearate, 3908
Aluminium—cobalt alloy, 0049
Aluminium—magnesium alloy, 0053
Benzoic acid, 2728
2,2-Bis(4-hydroxyphenyl)propane, 3679
Calcium silicide, 3937
Calcium stearate, 3890
2-Chlorobenzylidenemalononitrile, 3232
1,4-Diaminobenzene, 2364
2,6-Di-*tert*-butyl-4-cresol, 3684
3,3′-Dimethoxy-4,4′-diaminobiphenyl, 3653
Dimethyl terephthalate, 3286
3,5-Dinitro-2-toluamide, 2936
1,3-Diphenyltriazene, 3500
2,4-Hexadienoic acid, 2379
Hexamethylenetetramine, 2471
Magnesium, 4685
Magnesium—nickel hydride, 4458
Paraformaldehyde, 0416
Poly(ethylene), 0778
Silicon, 4903
Sucrose, 3552
Tetraphosphorus decasulfide, 4872
Thorium dihydride, 4483
Titanium, 4913
Titanium carbide, 0558
Titanium dihydride, 4484
Zinc stearate, 3891
Zirconium, 4922

See FLOUR, METAL SULFIDES, MISTS
See also DEFLAGRATION TO DETONATION, GEOMETRY OF VESSELS AND PIPEWORK

Methane

Reeh, D., *Chem. Abs.*, 1979, **90**, 126799

Tests on the explosive behaviour of combustible dust—methane—air mixtures in a 45 mm pipeline 200 m long showed that presence of a little fuel gas could cause combustible but non-explosive dusts to become unexpectedly hazardous.

See CARBONACEOUS DUSTS, DUSTS, METAL DUSTS

DUSTS

1. Taubkin, S. I. *et al., Chem. Abs.*, 1976, **85**, 110611
2. Leuschke, G., *Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 2, 647—656, Basle, SSCI, 1980
3. *NFPA 654*, Quincy (Ma), National Fire Protection Association, 1988
4. *Spec. Publ. - R. Soc. Chem.*, 2001, **268**, 11

A new method of classifying hazardous dusts into the 3 groups, highly explosible, explosible and fire-hazardous was proposed, based on lower explosive limits and maximum rate of pressure increase. An extension of the system to classify workrooms taking account of their volumes was also suggested [1]. The dependency of induction time (time until critical self-heating occurs) upon storage temperature and volume of dusts stored at or above their ignition temperatures has been studied [2]. A new US fire code covers prevention and control of fires and dust explosions in the chemical, dyestuffs, pharmaceutical and plastics industries [3]. A guide to assessing risks in an actual industrial environment is given [4].

DYES

1. Mizgireva, S. B., *Chem. Abs.*, 1987, **106**, 139802
2. Vasin, A. Ya. *Chem. Abs.*, 2004, 141, 412434m
3. Rossbach, V. *et al., Ger. Offen.* DE 19,650,252, 1996

In a DTA study of 14 anthraquinone dyes, most had high flash points (225—335°C) and ignition points (320—375°C). Purpurin dianilide [107528-40-5] was exceptional with the much lower values of 110 and 155°C, respectively [1]. A similar study of indigo type dyes and vat solubilised modifications is reported. The basic dyes decompose over 350°C, destabilised to around 200°C for solubilised dyes. The relation between functional groups, structure and flammability is discussed [2]. Sulfonyl azides have been employed for attachment of reactive dyes, it is claimed they are safer used in supercritical carbon dioxide than in water [3].

See also PYRAZOLONE DYESTUFF PREPARATION, SULFUR BLACK

EARTHQUAKE

1. Pine, S. H., *Chem. Health & Safety*, 1994, **1**(2), 10.
2. Yoshida, T., *Safety of Reactive Chemicals*, Chapt 9, Amsterdam, Elsevier, 1987
3. Yoshida, T. *et al.*, *Safety of Reactive Chemicals and Pyrotechnics*, p44, Amsterdam, Elsevier, 1995

Discussions, based on experience, of the measures needed to protect laboratories and equipment in earthquake zones.

Earthquakes provide the ultimate test of the storage of incompatible chemicals and are sometimes followed by fires in chemical stores. Very few causes of ignition are found: alkali metals; halogen oxysalts in conjunction with strong acids; and sulphuric or nitric acid and cellulose (wood flooring). These usually then ignite vapours of flammable solvents.
See STORAGE OF CHEMICALS

ELECTRIC FIELDS

Kabanov, A. A. *et al., Russ. Chem. Rev.*, 1975, **44**, 538—551
Application of electric fields to various explosive heavy metal derivatives (silver oxalate, barium, copper, lead, silver or thallium azides, or silver acetylide) accelerates the rate of thermal decomposition. Possible mechanisms are discussed.

ELECTROLYSIS

Mason, J. P., personal communication, 1999
Electrolysis is a means of putting energy into a chemical system. That energy may be stored in the system, to emerge spontaneously later. Apparently innocuous systems can thereby become extremely hazardous. The obvious example is the cleavage of water to produce an explosive mix of hydrogen and oxygen. There are more subtle risks: the performance of an electrode design was being tested over several weeks in a solution of ammonium chloride, topped up daily with ammonia. After about three weeks, the technician who topped up the beaker containing the assembly found its contents flying past his ears. No substantial piece of the beaker was ever found. That was trichloroamine formation, and destruction. Other nitrogenous compounds, in other halide electrolytes, could behave similarly.
See Ammonium chloride, Deuterium oxide
See also BATTERIES

ELECTRON BEAM MELTING

Brinza, V. N. *et al., Chem Abs.*, 1987, **106**, 22657
Potential hazards associated with electron beam vacuum melting of metals include the possibility of ignition of metal aerosols or condensate films in the event of sudden loss of vacuum at elevated temperatures.

ELECTROSTATIC HAZARDS

1. Haase, H., *Electrostatic Hazards: Evaluation and Control*, Weinheim, Verlag Chemie, 1977
2. Anon., *Loss Prev. Bull.*, 1979, (029), 134—138
3. Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 4—6
4. Anon., *Loss Prev. Bull.*, 1980, (035), 1—5
5. Maksimov, B. K. *et al., Chem. Abs.*, 1982, **96**, 165336
6. Anon., *Jahresber.*, 1985, 70—72
7. Wilson, N., *Chem. Abs.*, 1986, **105**, 138978
8. Jury, E., *Safety aspects and measures in electrostatic gas purification*, DECHEMA Monogr. 107, 1987, 383—388

9. Pay, F. J., *Loss Prev. Bull.*, 1987 (078), 1—8
10. Cartwright, P., *Chem. Engr.* (Rugby), 1988, (454), 49
11. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203
12. Astbury, G. R., *Org. Proc. Res. & Dev.*, 2002, **6**(6), 893

The comprehensive text contains numerous case studies and quantitative calculations on many aspects of static electrical hazards [1]. Case histories involving leakage of steam or other pressurised fluid, flow to or from storage tanks, dusts and unearthed plant segments are discussed [2]. In a group of 7 incidents involving fire or explosion, the common ignition source was static generated by pouring fine solids from plastic bags or through non-conducting ducts or funnels [3]. Seven further case histories involving fires or explosions in dusts or powders under various circumstances are detailed [4]. Equations for calculating maximum flow rates to avoid static build up during transfer of petroleum products to or from road or rail tanks have been derived [5].

In the preparations during unsettled weather for a large outdoor firework display, the pyrotechnic components, together with the starting fuses, electric igniters and charged batteries were all stored in the same building. The batteries were to be protected from the weather by wrapping in polythene film, and when this was unreeled, static discharge led to ignition of the stored materials, and uncontrolled fires and explosions destroyed the building [6]. Factors affecting incendiary behaviour of static spark discharges from the human body on ignition of methane— and hydrogen—air mixtures are discussed [7]. Safety aspects and precautionary measures to prevent fire and explosion in electrostatic gas purifiers are discussed [8]. A brief survey of the phenomenon, consequences and hazards of electrostatic charging in industrial operations is illustrated by case histories [9]. Accidents originating from static charge generation during the pouring of powder from polythene-lined fibreboard drums, or when digging dry cake from a vacuum filter bed dryer are analysed, and preventive measures proposed [10]. Poorly designed fire extinguishing systems may also lead to static hazards. A specialised mechanism for ignition of oxygen-rich atmospheres by electrostatic effects generated by bursting oxygen bubbles is postulated [11], and the detailed implications considered [12]. It might just occur in large (but not small) laboratory glassware, but has almost certainly been the cause of several fatalities at industrial scale, the oxygen bubbles usually coming from decomposing hydrogen peroxide.

See Carbon dioxide: Flammable materials
See other IGNITION SOURCES

ENDOTHERMIC COMPOUNDS

1. Weast, 1979, D61—84; *ibid.*, 2001, **5** 1-60
2. Mellor, 1941, Vol. 1, 706—707
3. Stull, 1977, 8—10

Most chemical reactions are exothermic, but indirect or high temperature reactions permit preparation of high energy product(s) which are known as endothermic (or energy-rich) compounds. Such compounds are thermodynamically unstable, because heat would be released on decomposition to their elements. The majority of endothermic compounds possess a tendency towards instability and possibly to explosive decomposition under various circumstances of initiation. Often, endothermic compounds possess features of multiple bonding ('unsaturation'), as in acetylene, hydrogen cyanide, silver fulminate, mercury azide or chlorine dioxide. Other singly bonded endothermic compounds are hydrazine, diborane, dichlorine monoxide, or nitrogen trichloride.

Many, but not all, endothermic compounds have been involved in violent decompositions, reactions or explosions, and in general, compounds with significantly positive values of standard heat of formation may be considered suspect on stability grounds. Notable exceptions are benzene and toluene (ΔH_f° +82.2, 50.0 Kj/mol; 1.04, 0.54 Kj/g, respectively), where there is the resonance stabilising effect of aromaticity; some azines not known to show instability are still more endothermic (pyridine 1.3; pyrazine 1.8 kJ/g). Values of thermodynamic constants for elements and compounds are tabulated conveniently [1], but it should be noted that endothermicity may change to exothermicity with increase in temperature [2]. There is a more extended account of the implications of endothermic compounds and energy release in the context of fire and explosion hazards [3]. Many examples of endothermic compounds will be found in the groups below. The individually indexed endothermic compounds, for most of which heats of formation are given in the text:

† Acetonitrile, 0755
* Ammonium hexacyanoferrate(II), 2572
† Arsine, 0100
Azido-2-butyne, 1469
3-Azidopropyne, 1111
cis-Azobenzene, 3478
Azoxybenzene, 3479
Barium azide, 0214
Benzenediazonium nitrate, 2268
Benzotriazole, 2262
Borane, 0135
Bromine azide, 0256
† 3-Bromopropyne, 1087
† 1,2-Butadiene, 1475
† 1,3-Butadiene, 1476
† Buten-3-yne, 1419
† 1-Butyne, 1477
† 2-Butyne, 1478
Cadmium azide, 3951
Cadmium cyanide, 0585
Cadmium fulminate, 0586
Cadmium nitride, 3954
Calcium azide, 3930
† Carbon disulfide, 0557
Chlorine dioxide, 4036
Chloroacetylene, 0648

Chloryl perchlorate, 4098
Copper(I) azide, 4281
Cyanamide, 0403
3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2626
Cyanoform, 1379
Cyanogen bromide, 0312
Cyanogen chloride, 0322
Cyanogen fluoride, 0337
† Cyclopropane, 1193
Diazene, 4463
2,3-Diazido-1,3-butadiene, 1433
Diazomethane, 0405
† Diborane(6), 0166
Dichlorine oxide, 4089
Dichlorine trioxide, 4094
1,4-Dicyano-2-butene, 2304
† Dicyanoacetylene, 1795
Dicyanofurazan, 1797
Dicyanofurazan *N*-oxide, 1798
† Dicyanogen, 0992
Diethylcadmium, 1671
Difluorodiazene, 4308
Diiodomethane, 0399
Dimethylcadmium, 0890
Dimethylmercury, 0903
Dimethylzinc, 0931
Dinitrogen oxide, 4739
Dinitrogen tetraoxide, 4720
Dioxygen difluoride, 4314
* *trans*-1,2-Diphenylethylene, 3636
Fluoroacetylene, 0658
Gold(III) oxide, 0115
1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine, 4789
Hydrogen azide, 4435
† Hydrogen selenide, 4480
† Hydrogen telluride, 4482
Iodoform, 0375
Lead(II) azide, 4776
Lead(IV) azide, 4784
Mercury(II) cyanide, 0972
Mercury(II) fulminate, 0974
* Mercury(II) thiocyanate, 0975
* Methyl isocyanide, 0756
† 3-Methyl-1,2-butadiene, 1886
† 2-Methyl-1,3-butadiene, 1887
† 3-Methyl-1-butyne, 1888

Nickel(II) cyanide, 0993
Nitrogen oxide, 4719
Nitrogen trichloride, 4137
Nitrogen triodide, 4628
Nitrosyl chloride, 4017
Nitryl chloride, 4019
Nitryl hypofluorite, 4298
Oxygen difluoride, 4311
† Pentaborane(9), 0188
† 1,4-Pentadiene, 1891
† 1,3-Pentadiene, 1890
† 1,2-Pentadiene, 1889
† 2-Pentyne, 1893
† 1-Pentyne, 1892
Perchloryl perchlorate, 4101
† Phosphine, 4503
* Phosphorus triazide oxide, 4782
Potassium hexacyanoferrate(III), : Hydrochloric acid, 2057
† Propadiene, 1121
Propadienedithione, 1346
† Propyne, 1122
Silicon tetraazide, 4785
Silver azide, 0023
Silver cyanide, 0298
Silver fulminate, 0300
* Sodium hexaazidophosphate, 4788
† Stibine, 4505
Strontium azide, 4779
Styrene, 2940
Tetracyanoethylene, 2625
Tetraethyllead, 3089
Tetramethyl-2-tetrazene, 1753
Tetrasulfur tetranitride, 4764
* Tetravinyllead, 3011
Tetrazole, 0410
* Thallium(I) tetraazidothallate, 4786
* 2,4,6-Trichloro-1,3,5-triazine, 1035
* Vinyl isocyanide, 1106
Zinc cyanide, 1000
ACETYLENIC COMPOUNDS
ALKYLMETALS
ALKYNES
AZIDES
BORANES
CYANO COMPOUNDS
DIENES

HALOACETYLENE DERIVATIVES
HALOGEN OXIDES
METAL ACETYLIDES
METAL FULMINATES
OXIDES OF NITROGEN

ENERGETIC COMPOUNDS

1. Witucki, E. F. *et al., J. Chem. Eng. Data*, 1983, **28**, 285—286
2. Various, *Mater. Res. Soc. Proc.* (418), 1996
3. Sikder, A. K. & N., *J. Haz. Mat.* 2004, **112**(1-2), 1

Syntheses of 5 energetic aliphatic azido compounds are described: caution is necessary in handling these because of their impact-sensitivity [1]. A later symposium on energetic materials, here meaning explosives and propellants, is reported [2]. The same meaning is carried in the paper [3]. Individual compounds listed are:

6-Azidohexyl 6-azidohexanoate, 3545
Bis(2-azidoethoxymethyl)nitramine, 2475
N-Butyl-*N*-2-azidoethylnitramine, 2523
1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane, 3044
Tris(2-azidoethyl)amine, 2476

See also ENDOTHERMIC COMPOUNDS, FLUORODINITROMETHYL COMPOUNDS (reference 6)

ENVIRONMENTALISM

1. Kletz, T. A., *Chemical Engineer*, 1992, 527, 38
2. Kletz, T. A., *Process Safety Progr.*, 1993, **12**(3), 147
3. Förster, H. *et al., Ber. Dtsch. Wiss. Ges.; Erdöl, Erdgas, Kohle Forschungsber.*, 1994, 462
4. De Haan, J. D. *et al., Proc. Int. Conf. Fire. Safety*, 1995, **20** 67
5. Hofelich, T. C. *et al., Proc. 33rd Annu. Loss Prev. Symp.*, 1999, 5a-1
6. Anderson, S. E. *et al., Process Safety Progr.*, 2000, 19(1), 5
7. Ozog, H. *et al., Process Safety Progr.*, 2000, 19(1), 25
8. Rowe, S., Personal conversation, 2004
9. Kaupp, G. *et al., Chem. - Eur. J.*, 2002, **8**(6), 1395
10. Crawley, F. K. et al., *J. Haz. Mat.*, 2002, **93**(1), 17
11. U.S. Dept. of Health and Human Services, Alert, April 2000
12. Walker, C., *Industrial Fire World*, 1997, Nov/Dec

Environmentalists react violently to the mere word chemical. Some cases where Green and naÿve over-reaction has led to environmental damage and accompanying human fatalities from explosion are described and some likely causes of future mishap suggested [1,2]. It is proposed to lower the permitted vapour pressure of gasoline, to reduce environmental release of Volatile Organic Compounds, which will bring the headspace of car fuel tanks below the upper explosive limit on cool mornings [3]. Consideration is given to the increased fire risk of household aerosols associated with use of liquid petroleum gases and dimethyl ether as environmentally friendly propellants [4]. Models for balancing Safety and Environment in the petrochenical industry have been offered [10]. Use of carbon beds to remove pollutant vapours from air has often led to fires in those beds. Studies aimed at preventing this are reported [5,7]. Accidents in these and other emission control devices are discussed in [6]. Nature meant dung to be scattered on land, this was once done with sewage but is now thought pollution. Drying sewage sludge for incineration produces considerable dust-explosion hazards [8].

Generation and use of habitually explosive solid diazonium salts, the use by cautious grinding with coupling reagents, is advanced on waste-minimisation grounds [9]. The limits for release to atmosphere of ethylene oxide, used for medical sterilisation, have been tightened beyond what scrubbers can achieve, so catalytic off-gas oxidation units were added by several users. The oxide has very wide flammable limits and very low ignition energy. The result has been several explosions when scrubbers were removed, bypassed or ineffective, sending rich mixes to the oxidation units — where oxidation did not remain catalytic. Much structural damage, but fortunately no injuries, are reported [11]. An incident is reported in which firemen, cleaning up after a grocery chiller-unit fire, became ill. This was attributed to hydrogen fluoride created by pyrolysis of the environmentally safe hydrofluorocarbon refrigerant, which had replaced hydrogen-less chlorofluorocarbons [12].

See Hydrogen peroxide: Waste treatment

EPOXIDATION

Swern, 1971, Vol. 2, 428—533

Preparation of epoxides (oxirans) on the commercial scale as resin or polymer components is widely practised. Careful control of conditions is necessary to avoid hazards, and the several factors involved are reviewed.

See Peroxyformic acid: Organic materials
    Hydrogen peroxide: Unsaturated compounds, 4471

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

1,2-EPOXIDES

Pogany, G. A., *Chem. & Ind.*, 1979, 16—21

All factors relevant to the safe use of ethylene oxide and propylene oxide in high pressure bench scale experiments are detailed. Salient points include the need for a well-designed agitated reactor with adequate provision for reaction heat removal and emergency pressure relief; prevention of back-flow from reactor to oxide storage vessels; avoidance of a reaction atmosphere of 100% ethylene oxide vapour and/or presence of air; avoiding an excess of oxide. The 3 lower members of this group of compounds are bulk industrial chemicals, and their high reactivity has been involved in several serious incidents.

Individually indexed compounds are:

1-Allyloxy-2,3-epoxypropane, 2428
2,2-Bis[4(2′,3′-epoxypropoxy)phenyl]propane, 3819
1,4-Bis(2,3-epoxypropoxy)butane, 3347

† 1-Chloro-2,3-epoxypropane, 1158
† Cyclopentene oxide, 1900
2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane, 2291
2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane, 2332
† 1,2:3,4-Diepoxybutane, 1524
endo-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene, 2329
Endrin, 3453
† 1,2-Epoxybutane, 1604
† 3,4-Epoxybutene, 1517
2,3-Epoxypropanol (Oxiranemethanol), 1225
2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone, 3124
2,3-Epoxypropionaldehyde oxime (Oxiranecarboxaldehyde oxime), 1178
4(2,3-Epoxypropoxy)butanol, 2862
* 2,3-Epoxypropyl nitrate, 1182
3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2397
† Ethylene oxide, 0825
† 1-Fluoro-2,3-epoxypropane, 1167
Glycidyl azide, 1187
Nitrilotris(oxiranemethane), 3175
† Propylene oxide, 1221
Tetrafluorooxirane, 0628
† Thiirane, 0836
1,3,5-Tris(2,3-epoxypropyl)triazine-2,4,6-trione, 3527
See other STRAINED-RING COMPOUNDS

Dinitrogen pentaoxide
See Dinitrogen pentaoxide: Strained-ring heterocycles

Nitronium perchlorate
See Nitronium perchlorate: 1,2-Epoxides

EQUATIONS

Editor's comments

Balance them! The editor has frequently found chemists fresh from university blithely ignoring evolution of gaseous byproducts, such as carbon monoxide and methyl halides, capable of rupturing vessels and killing operators. Write them step by step too, this may reveal mechanistic and catalytic effects harmful to chemist, cost or yield.

See also NITRATION INCIDENTS

ETHERS

1. Jackson, H. L. *et al., J. Chem. Educ.*, 1970, **47**, A175
2. Davies, A. G., *J. R. Inst. Chem.*, 1956, **80**, 386—389
3. Dasler, W. A. *et al., Ind. Eng. Chem. (Anal. Ed.)*, 1946, **18**, 52
4. Hazardous Chemicals: Information and Disposal Guide, 1984, 87, 91, 98, 265

5. Robertson, R., *Chem. & Ind.*, 1933, **52**, 274
6. Morgan, G. T. *et al., Chem. & Ind.*, 1936, **55**, 421—422
7. Williams, E. C., *Chem. & Ind.*, 1936, **55**, 58—581
8. Karnojitsky, V. J., *Chim. et Ind.* (Paris), 1962, **88**, 233—238
9. Unpublished observations, 1973
10. Schwartz, A. M., *Chem. Eng. News*, 1978, **56**(24), 88

There is a long history of laboratory and plant fires and explosions involving the very high flammability and/or tendency to peroxide formation in these widely used solvents, diisopropyl ether being the most notorious. Methods of controlling peroxide hazards in the use of ethers have been reviewed [1], and information on storage, handling, purification [2,3] and disposal [4] have been detailed.

Three violent explosions of diisopropyl ether had been reported [5,6] and a general warning on the hazards of peroxidised ethers had been given by 1936 [7]. The latter reference mentions diethyl, ethyl *tert*-butyl, ethyl *tert*-pentyl and diisopropyl ethers as very hazardous, while methyl *tert*-alkyl ethers, lacking non-methyl hydrogen atoms adjacent to the ether link, are relatively safe. Bis(2-methyl-2-propen-1-yl) ether ('dimethallyl ether') is unusual in that although it forms peroxides with extreme rapidity, these are thermolabile and are progressively destroyed without danger during distillation [7]. For like reasons, the slower distillation enforced by industrial scale partly explains why peroxidation induced explosions are essentially laboratory accidents only. The mechanism of peroxidation of ethers has been reviewed [8].

When solvents have been freed from peroxides by percolation through a column of activated alumina, the adsorbed peroxides must promptly be desorbed by treatment with the polar solvents methanol or water, which should be discarded safely. Small columns used to deperoxidise diethyl ether or tetrahydrofuran were allowed to dry out by evaporation. When moved several days later, the peroxide concentrated on the alumina at the top of the columns exploded mildly and cracked the glass columns [9].

A procedure for preparation of dry oxygen-and peroxide-free low boiling ethers (diethyl ether, THF, dioxane, glyme etc.) is described which involves distillation from sodium diphenylketyl.

See Nitrogen oxide: Sodium diphenylketyl for care in disposal of the sodium—ketyl residues.

Individually indexed compounds include:

† Allyl ethyl ether, 1949
1-Allyloxy-2,3-epoxypropane, 2428
† Bis(2-ethoxyethyl) ether, 3071
Bis-(2-methoxyethyl) ether, 2544
† Butyl ethyl ether, 2535
† Butyl methyl ether, 2004
† *tert*-Butyl methyl ether, 2005
† Butyl vinyl ether, 2478
† Cyclopropyl methyl ether, 1603
Di(2-propynyl) ether, 2320
† Diallyl ether, 2425

Dibenzyl ether, 3648
† Dibutyl ether, 3066
† 1,1-Diethoxyethane, 2540
† 1,2-Diethoxyethane, 2541
† 3,3-Diethoxypropene, 2854
† 2,3-Dihydrofuran, 1514
† Diisopropyl ether, 2537
† 1,2-Dimethoxyethane, 1695
† 1,1-Dimethoxyethane, 1694
† Dimethoxymethane, 1277
† 3,3-Dimethoxypropene, 1962
1-(1,1-Dimethylethoxy)-2-methylpropane, 3067
1-(1,1-Dimethylethoxy)-2-methylpropane, 3067
† 1,3-Dioxane, 1611
† 1,4-Dioxane, 1612
† Dipropyl ether, 2538
† Divinyl ether, 1516
1-Ethoxy-2-propyne, 1903
2-Ethoxyethanol, 1696
† Ethyl isopropyl ether, 2006
† Ethyl propenyl ether, 1950
† Ethyl vinyl ether, 1605
† Furan, 1435
† Isopropyl vinyl ether, 1951
* Methoxy-1,3,5,7-cyclooctatetraene, 3143
2-Methoxyethanol, 1280
† 2-Methoxyethyl vinyl ether, 1967
† Methyl vinyl ether, 1217
† 2-Methyltetrahydrofuran, 1955
† Tetrahydrofuran, 1607
† Tetrahydropyran, 1959
See other PEROXIDISABLE COMPOUNDS

ETHOXYETHYNYL ALCOHOLS $EtOC{\equiv}CCR_2OH$

1. Arens, J. F., *Adv. Org. Chem.*, 1960, **2**, 126
2. Brandsma, 1971, 12, 78

Vigorous decompositions or violent explosions have been observed on several occasions during careless handling (usually overheating) of ethoxyethynyl alcohols (structures not stated) [1]. The explosions noted when magnesium sulfate was used to dry their ethereal solutions were attributed to the slight acidity of the salt causing exothermic rearrangement of the alcohols to acrylic esters and subsequent explosive reactions (or polymerisation). Glassware used for distillation must be pretreated with ammonia to remove traces of acid [2].

See 4-Ethoxy-2-methyl-3-butyn-2-ol
See other ACETYLENIC COMPOUNDS

EXOTHERMIC DECOMPOSITION REACTIONS

1. Grewer, T., *Proc. 2nd Int. Symp. Loss Prev. Safety Prom. Process Ind.*, III-105—113, 539, Frankfurt, Dechema, 1978
2. Grewer, T., *Chem. Ing. Tech.*, 1979, **51**, 928—933
3. Grewer, T., *Runaway Reactions*, 1981, Paper 2/E, 1—18

Problems in relating chemical structure to the type and course of exothermic decomposition are discussed, with an outline of some general methods useful in following the course of such reactions. Comparative figures for the temperature of onset of decomposition for typical molecular groupings which confer instability are tabulated and the mutual effects of the presence of two such groupings are discussed [1]. The role played by undesired or unexpected reactions in leading to the development of hazards in chemical processing operations is discussed. Typical decomposition energies are assigned to ‘unstable’ molecular groupings. The results of DTA examination are compared with warm storage tests, and the effects of various substituents and of other substances on the stability of particular compounds are studied [2]. The use of relatively simple tests, either at atmospheric or elevated pressures, to assess the hazards of exothermic decomposition reactions by determining the quasi-adiabatic self-heating curves and induction times are described in detail [3].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

EXOTHERMICITY

Craven, A. D., *Hazards from Pressure*, IChE Symp. Ser. No. 102, Oxford, Pergamon, 1987

A simplified method for near-quantitative estimation of the exothermicity (energy of exothermic decomposition/unit mass) of products or reaction mixtures, which is suitable for a hand-calculator, is presented. It is based on the difference between the total energies of atomization of all the bonds in the starting material(s) and of those in the likely products of decomposition or reaction, rather than on the group contribution methods used with computer programs, which are more accurate but more complex. Examples are given which show the accuracy of the method to be sufficient for preliminary assessment of potential hazards, together with tabulated values of average bond energies sutable for the purpose.

See also COMPUTATION OF REACTIVE CHEMICAL HAZARDS, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

EXOTHERMIC REACTION MIXTURES IN STEEL MAKING

Babaitsev, I. V. *et al., Chem. Abs.*, 1987, **107**, 138866

Minimum impact energies to initiate the explosion of various exothermic mixtures, used for the continuous casting of steel, were determined. Components used included sodium nitrate, aluminium—iron scale, silicocalcium, ferrosilicon; fluorspar, borax, etc. Hazardous mixtures were defined, and improved safety controls were derived.

EXPLOSIBILITY

1. Lothrop, W. C. *et al., Chem. Rev.*, 1949, **44**, 419—445
2. Tomlinson, W. R. *et al., J. Chem. Educ.*, 1950, **27**, 606—609
3. Coffee, R. D., *J. Chem. Educ.*, 1972, **49**, A343—349; *Chemical Stability*, Chapter 17 in *Safety & Accident Prevention in Chemical Operations*, Fawcett, H. H. & Wood, W. S. (Eds.), New York, Wiley, 2nd edn., 1982
4. Van Dolah, R. W., *Ind. Eng. Chem.*, 1961, **53**(7), 50A—53A
5. Stull, D. R., *Chem. Eng. Progr.*, 1973, **7**, 67—73; reprinted *J. Chem. Educ.*, 1974, **51**(1), A21—25
6. Spear, R. J. *et al., Rept. MLR-R-850, AR-003-031*, Richmond (Va.) USNTIS, 1982
7. Chahine, G., *Inform. Chim.* (Paris), 1987, (283), 141—143
8. Melhem, G. A. *et al., Process Safety Progr.*, 1996, **15**(3) 168
9. Paine, R. T. *et al., Inorg. Chem.*, 1999, **38**(16), 3788
10. Yoshida, T. et al., *Safety of Reactive Chemicals & Pyrotechnics*, Amsterdam, Elsevier, 1995
11. Chervin, S. *et al., Process Safety Progress*, 2003, **22**(4), 242

Explosibility may be defined as the tendency of a chemical system (involving one or more compounds) to undergo violent or explosive decomposition under appropriate conditions of reaction or initiation. Paradoxically, the first requirement of an explosive is stability — but only metastability. This can mean that what you performed without accident today may still blow your silly head off if repeated tomorrow. Even explosive mixtures must remain quiescent for long enough to achieve mixing if they are to pose a major hazard; should they blow each other apart on contact, no more than minor injuries are likely. It is obviously of great practical interest to be able to predict which compound or reaction systems are likely to exhibit explosibility (and the degree exhibited), and much work has been devoted to this end. Early work [1] on the relationship between structure and performance of 176 organic explosives (mainly nitro compounds or nitrate esters) was summarised and extended in general terms to multi-component systems [2]. The contribution of various structural factors (bond-groupings) was discussed in terms of heats of decomposition and oxygen balance of the compound or compounds involved in the system. Materials or systems approaching stoicheiometric composition (zero oxygen balance) are the most powerfully explosive, giving the maximum heat energy release. Bond groupings known to confer explosibility were classed as 'plosophores', and explosibility-enhancing groups as 'auxoploses' by analogy with dyestuffs terminology. The latter groups (ether, nitrile or oximino) tend to increase the proportion of nitrogen and/or oxygen in the molecule towards (or past) zero oxygen balance. (Although not directed at explosion, a similar table, lacking peroxides but including group heats of decomposition, appears in [11]).

Although the semi-empirical approach outlined above is of some value in assessing potential explosibility hazards, much more fundamental work has been done subsequently to institute a more quantitative basis for such assessment. A combination of thermodynamical calculations with laboratory thermal stability and impact-sensitivity determinations has allowed a system to be developed which indicates the relative potential of a given compound or reaction system for sudden energy release, and the relative magnitude of the latter [3]. A similar treatment, specifically for compounds designed or expected to be explosives, was developed earlier [4]. A further computational technique which took account of both thermodynamic and kinetic considerations permitted the development of a system which provides a numerical Reaction Hazard Index (RHI) for each compound, which is a real, rather than a potential, indication of hazard. The RHI's calculated for 80 compounds are in fairly close agreement with the relative hazard values (assessed on the basis or experience) assigned on the NFPA Reactivity Rating scale for these same compounds [5]. In the context of the preparation of highly energetic materials, developments in methods of prediction of explosive properties are discussed briefly [6]. Information on methods of predicting explosive instability in organic and organometallic compounds is included in a general survey of this topic [7]. It is suggestd that the Calculated Adiabatic Reaction Temperature, CART, the temperature the reaction products would attain under adiabatic containment is generally a better predictor of explosive risk than is the simple heat of reaction since it allows for the variable thermal capacities of the products. It is not too good for organic peroxides. Both techniques depend upon selecting the right decomposition reaction [8].

Practical means of determining the sensitivity of very explosive compounds, on milligram scale, are outlined [9]. A drop-weight test is judged by recorded sound energy (not entirely satisfactory, since dropping weights itself makes a noise — Editor). Electrostatic tests attuned to likely human charge are conducted by discharging 0.36 J from a needle at 15 kV through a sample, and friction by grinding between two (presumably unglazed) porcelain surfaces, under load.

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, COMPUTATION OF REACTIVE CHEMICAL HAZARDS, EXOTHERMIC DECOMPOSITION REACTIONS, OXYGEN BALANCE, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

EXPLOSIONS

1. Stull, 1977
2. Leiber, C. O. *et al.*, NATO Sci. Ser. 1, 1999, 26, 1

Fundamental factors which contribute to the occurrence of fire and explosions in chemical processing operations have been collected and reviewed in this 120-page book, which serves as an extremely informative guide to the whole and complex subject, subdivided into 12 chapters. These are: Introduction; Thermochemistry; Kinetochemistry; Ignition; Flames; Dust Explosions; Thermal Explosions; Gas Phase Detonations; Condensed Phase Detonations; Evaluating Reactivity Hazard Potential; Blast Effects, Fragments, Craters; Protection Against Explosions. There are also 3 Appendices, 153 references and a Glossary of Technical Terms [1]. An introductory historical overview of explosion incidents, with particular attention to non-chemical causes, has been published [2].

EXPLOSIVE BOILING

1. Vogel 1957, 4
2. Weston, F. E., *Chem. News*, 1908, 27

The hazards associated with the addition of nucleating agents (charcoal, porous pot, pumice, anti-bumping granules, etc.) to liquids at or above their boiling points have been adequately described [1]. The violent or near-explosive boiling which ensues is enhanced by gases adsorbed onto such solids of high surface area. Incidents involving sudden boiling of salt solutions being concentrated for crystallisation in vacuum desiccators have also been described. The heat liberated by rapid crystallisation probably caused violent local boiling to occur, and the crystallising dishes (soda glass) were fractured [2].

EXPLOSIVE COMBUSTION

1. Lafitte, P. *et al., Hautes Temp., Leurs Util. Phys. Chim.*, 1973, **1**, 1—40
2. Gardner, G., *Chemical Engineer*, 1994, (563), 153.

A comprehensive review includes autoignition of gas mixtures, explosions at low and high temperatures, properties of flames and combustion of metals [1]. A review of explosion suppression techniques for dust, mist or vapour deflagrations, as an alternative to venting industrial plant [2].

EXPLOSIVES

1. Federoff, 1960—1987
2. *Explosives, Propellants and Pyrotechnic Safety Covering Laboratory, Pilot Plant and Production Operations*: Manual AD-272-424, Washington, US Naval Ordnance Laboratory, 1962
3. Kirk-Othmer, 1980, Vol. 9, 561—671
4. Ullmann, 1990, A10, 143
5. Urbanski, 1964—1984, Vols. 1—4.
6. *Explosives* Köhler, J. & Meyer, R., Weinheim, VCH, (4th Edn), 1993

Explosive materials intended as such are outside the scope of this work and many, even of those in widespread use, do not have an entry. The 1990s have seen a surprising level of published research aimed at finding new military explosives, most of the molecules tested have not been given an entry: they are obvious members of dangerous groups, typically polynitro-compounds with other nitrogen functionality. Several specialist reference works on explosives contain much information relevant to their properties and safety practices for unstable materials.

FERROALLOY POWDERS **Fe—Mn, Fe—Si, Fe—Ti**

Barbaitsev, I. V. *et al., Chem. Abs.*, 1983, **99**, 161983

Explosion parameters have been measured for ferromanganese, ferrosilicon and ferrotitanium powders in a 1m^3 chamber. Maximum pressures of 2.8—3.9 bar, at maximum rates of rise of 8.9—21.8 bar/s were determined. Individual entries are:

Ferromanganese, 4383
Ferrosilicon, 4384
Ferrotitanium, 4385
See other ALLOYS

FERTILISER

1. Baccarani, C., *et al., Chem. Abs.*, 1992, **117**, 177392
2. Laing, M., *J. Chem. Educ.,* 1993, **70**(5), 392
3. Shah, K. *et al., Proc. Int. Fert. Soc.*, 2000, **448**, 1
4. Kiiski, H., *Proc. Int. Fert. Soc.*, 2000, **450**, 1
5. Tang, S-L. *et al., Chem. Abs.*, 2004, **140**, 377463a

Self-sustaining thermal decomposition of NPK fertilisers is apparently possible if crystalline potassium nitrate is present from a exchange reaction of ammonium nitrate [1]. Almost pure fertiliser grades of ammonium nitrate are legally restricted in some countries because of its instability [2]. An investigation of the (large) proportions of other fertiliser components needed to make ammonium nitrate undetonable has been made [5]. An extensive review of safety aspects of ammonium nitrate based compound fertilisers has been published [3]. So has a study of their thermal decomposition and the implications for storage [4].

See Ammonium nitrate

FINELY DIVIDED METALS

1. Manuev, N. V. *et al., Chem. Abs.*, 1979, **90**, 111642
2. Murdock, T. O., *Diss. Abs. Int. B*, 1978, (9), 1291

Requirements for safe storage of powdered Al, Hf, Mg, Ti, Zn and Zr are outlined. Fires are best extinguished with various fluxes, trimethyl boroxine, asbestos fines (!), talc, graphite, sodium chloride, soda ash, lithium chloride or powdered dolomite [1]. Slurries of Al, Cd, Cu, Ge, In, Ni, Pb, Sn or Zn produced by metal atom—solvent cocondensation at —196°C are extremely active chemically [2], and would be pyrophoric on exposure to air.

See Aluminium: Diethyl ether

See also METAL DUSTS

FIRE

1. *Fire Protection Handbook*, Quincy (Ma.), National Fire Protection Association, 16th edn., 1986
2. Fire Service Abstracts, (quarterly since 1981), Boreham Wood., Fire Research Station
3. Bahme, 1972
4. Meidl, 1972
5. *Fire and Related Properties of Industrial Chemicals*, London, Fire Protection Association, 4th edn., revised 1974
6. *Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids*, 325M, Quincy (Ma.), NFPA, 1984
7. *Matrix of Electrical and Fire Hazard Properties and Classification of Chemicals*, AD-A027 181/7GA, Richmond (Va.), USNTIS, 1975
8. *Fire Precautions in Chemical Plant: A Code of Practice*, BS 5908: 1980
9. *DH-HLH-88*, 1988; *NFPA 45*, 1986, Quincy (Ma), National Fire Protection Association

The handbook covers all aspects of fire protection and remedial measures, including those for involvement of chemicals in storage or in process operations [1]. The compilation of references to the scientific literature on fire has been renamed [2] and is now a quarterly publication subdivided and classified as previously. Further aspects, with examples of the special extinguishing problems arising from involvement of reactive chemicals in fires, are detailed [3,4]. The tabulated list of the physical and fire-hazardous properties of some 800 industrially significant chemicals [5] has a US counterpart covering 1300 materials [6]. A matrix relates fire hazardous properties of 226 commercial chemicals to the classification groups of the US National Electrical Code [7]. A UK Code of Practice is applicable to all chemical industry [8], and two US fire codes cover electrical installations in hazardous locations, and requirements for chemical-using laboratories, respectively [9].

FIRE EXTINGUISHERS

1. *Fire Safety Data Sheets 6001*—6003, London, Fire Protection Association
2. Hirst, R., *Chem. Engr.*, 1974, 627—628, 636
3. Anon., *Loss Prev. Bull.*, 1978, (022), 107—113
4. Webster, J. M., *Fire Surveyor*, 1984, **13**(2), 5—7
5. Hird, D., *Fire Prev.*, 1987, (202), 20—26

Three illustrated data sheets cover the choice; siting, care and maintenance; and use of portable fire extinguishers [1]. Detailed accounts of modern extinguishing agents and their use in chemical environments are available [2,3]. Of 3 types of multipurpose hand extinguishers tested comparatively (multipurpose powder, halon, and spray foam), the latter provides higher efficiency for a lower level of skill [4]. In a review of foam applications, a list of flammable liquids which destroy the blanketing effect is given. The most adverse effects are shown by ethylamine and isopropylamine, while several esters, ketones, alcohols and glycols have but slight effects on foam stability [5].

FLAMMABILITY

1. Coward, H. F. *et al., Limits of Flammability of Gases and Vapours*, Bull. 503, Washington, US Bur. Mines, 1952
2. Zabetakis, M. G., *Flammability Characteristics of Combustible Gases and Vapours*, Bull. 627, Washington, US Bur. Mines, 1965
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7. Mullayanov, F. I. *et al., Chem. Abs.*, 1978, **89**, 91976
8. Ducros, M. *et al., Thermochim. Acta*, 1981, **48**, 351—359
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14. Hodo, H. *et al., Int. Chem. Eng.*, 1987, **27**(4), 709—715
15. Zetsepin, V. M., *Chem. Abs.*, 1988, **109**, 98069
16. Ducros, M. *et al., J. Haz. Mat.*, 1988, **19**, 33—49
17. Mulzyczuk, J., *Chem. Abs.*, 1989, **110**, 12860
18. Lihou, D., *J. Loss Prevention*, 1993, **6**(4), 266
19. Barfuss, S. *et al., Arch. Combust.*, 1993, **13**(1-2), 33
20. Melhem, G. A., *Process Safety Progr.*, 1997, **16**(4), 203
21. De Smedt, G., *et al., J. Hazard. Mat.*, 1999, **70**(3), 105
22. Grosshandler, W. *et al., J. Heat Transfer*, 2000, **122**(1), 92
23. Wierza, I, *et al., Chem. Abs.*, 2000, **132**, 539646t
24. Kondo, S. *et al., J. Haz. Mat.*, 2001, **82**(2), 113
25. Ural, E. A., *Proceedings of the Annual Loss Symposium*, 2002, (36th), Amer. Inst. Chem. Eng., 279
26. Fomin, P. A. *et al., Adv. In Confined Detonations*, 2002, 167
27. Britton, L. G., *Proceedings of 36th Annual Loss Prevention Symposium*, 2002, 92, Amer. Inst. Chem. Eng.
28. Britton, L. G., *Proceedings of 36th Annual Loss Prevention Symposium*, 2002, 161, Amer. Inst. Chem. Eng.
29. Klaubert, M., *Chem. Ing. Technik*, 2004, **76**(7), 933

The hazards associated with flammability characteristics of combustible gases and vapours are excluded from detailed consideration in this Handbook, since the topic is adequately covered in standard reference works on combustion, including the 2 sources of much of the data on flammability limits [1,2].

However, to reinforce the constant need to consider flammability problems in laboratory and plant operations, the flammability (or explosive) limits have been included (where known) for those individual substances with flash points below 25°C. With the few noted exceptions, explosive limits quoted are those at ambient temperature and are expressed as % by volume in air in Appendix 2.

Semi-empirical formulae, based only on molecular structure, have been derived which allow flammability limits to be calculated for hydrocarbons and alcohols. Flash points, autoignition temperatures and boiling points may also be calculated from molecular structure for these classes. Quoted examples indicate the methods to be reasonably accurate in most cases [3]. Equations are given for calculating upper and lower flammability limits of 102 organic compounds (hydrocarbons, alcohols, ethers, esters, aldehydes, ketones, epoxides, amines and halides) from structure and stoicheiometry in air [4]. The HC value (Hazardous Concentration, the ratio of the concentration of a substance to its lower flammable limit in the same units) is useful in estimating flammable limits of mixtures of combustible gases [5]. Equations have been derived to calculate the LEL for an organic compound as a function of the number of carbon atoms, the heats of formation of the compound and of an alkane of the same carbon number, state of aggregation, etc., [6], and for petroleum products and their components [7].

The criteria defined by the CHETAH program (*see* COMPUTATION OF HAZARDS) were used to predict lower and upper flammable limits for various organic (C,H,O,N) compounds, results generally being in good agreement with experimental values [8].

A method for predicting upper flammable limits for C_1—C_8 hydrocarbons has been developed [9]. Determination of flammability limits in a spherical container, rather than in the traditional vertical tubes tends to show rather wider values than the tube method for methane to pentane, and for ethylene. It is proposed that these wider limits are more realistic in practice, and especially for purging purposes in significant volumes [10]. Comparison of 20 litre sphere and DIN methods for determining flammable limits showed some noticeable differences for upper explosive limit [21]. An apparatus is described for determining flammability limits for marginally flammable materials such as difluoromethane is described, relying upon extinction rather than ignition of a flame [22]. A critique and comparison of the various methods in use for measuring flammable limits has been published. It is claimed that the European methods give too wide a range (which others might hold is playing safe) [27]. Another concept of relevance in the context of flammability and extinguishment is that of the minimum oxygen content necessary to support combustion. The Oxygen Index is a quantified measure of this, and is becoming of widespread use for non-volatile flammable solids of many types [11].

A group contribution method has been developed to predict upper flammability limits for pure organic compounds. It is applicable to many homologous series which can be constructed from the groups included, and a procedure is given for calculating the confidence limits of the predictions [12]. The use of a microcomputer to estimate flammability limits for organic compounds is described, based on MW and functional groups present. Estimated LELs agreed well with published data, but there was some deviation in UELs [13]. Factors affecting propagation and quenching of flames in cylindrical pipes were investigated experimentally to establish design criteria for flame arresters. Critical velocity to assure flame quenching was below 5 m/s for an open-sided (venting) arrester, or rather higher when the arrester is inside a pipe [14]. Equations relating upper flammability limits to lower limits have been derived for hydrocarbons. From an experimental or calculated lower limit, the upper limit can be predicted with good accuracy [15]. Use of the CHETAH program to determine the flammability of organic oxygen compounds and to estimate their lower flammability limits has been described [16]. A method of calculating lower and upper flammability limits for complex gas mixtures, based on Le Chatelier's law, is described [17]. However, an experimental study of hydrogen and hydrocarbon mixes did not always agree with this law. At higher start temperatures flammability of hydrogen and methane showed variance with residence time [23]. It is claimed that better results are obtained if oxidation rates, as well as molar proportions, are considered for mixtures [29]. A procedure for calculating flammable limits of vapour/air mixes under reduced pressure and with nitrogen enrichment, for safe industrial drying operations, is reported [18]. Prediction of flammable limits, for both pure materials and mixtures in air or oxygen, is attainable by way of theoretical flame temperatures. If these are below 1000—1500°C, the mixture should be non-flammable [20]. Essentially similar is the use of heats of oxidation to predict flammable limits [28]. Another method using semi-empirical F-nos is advanced to calculate explosive limits, including those for mixtures [24]. It is reported that bubbles of air or oxygen in flammable liquids can be ignited even at pressures too high for the bubble to be within conventional explosive limits [19]. A study of bubble ignition, concentrating on oxygen in cyclohexane is reported [26].

Flammability limits change with pressure. It is reported that many halocarbon fire extinguishants form flammable mixtures with air at elevated pressure [25].
See OXYGEN INDEX (reference 5)
See also OXYGEN ENRICHMENT

FLASH POINTS

1. *Flash Points*, Poole, BDH Ltd., 1962
2. 'Catalogue KL4', Colnbrook, Koch-Light Laboratories, Ltd., 1973
3. *Flash Point Index of Trade Name Liquids*, 325A, Quincy (Ma.), NFPA, 1972
4. *Properties of Flammable Liquids*, 325M, Quincy (Ma.), NFPA, 1969
5. Prugh, R. W., *J. Chem. Educ.*, 1973, **50**, A85—89
6. Shimy, A. A., *Fire Technol.*, 1970, **6**(2), 135—139
7. Thorne, P. F., *Fire Mater.*, 1976, **1**, 134—140
8. Magdanz, H., *Plaste Kautsch.*, 1977, **24**, 774—777
9. Li, C. C. *et al., J. Fire Flamm.*, 1977, **8**, 38—40
10. Tiedtke, K. H., Ger. Offen., 2 723 157, 1978
11. Saborowska-Szpyrkowa, I. *et al., Chem. Abs.*, 1979, **90**, 189290; 1981, **95**, 64598
12. Gmehling, J. *et al., Ind. Eng. Chem. Fundam.*, 1982, **21**, 186—188
13. Shebeko, Yu. N. *et al., Chem. Abs.*, 1983, **98**, 184837
14. Gooding, C. H., *Chem. Eng. (Intern. Ed.)*, 1983, **90**(25), 88
15. Bodinelli, L., *Chem. Eng. News*, 1982, **60**(28), 4
16. MacDermott, P. E., *Chem. Brit.*, 1974, **10**, 228
17. Mitsui, T., *Chem. Abs.*, 1987, **107**, 222429
18. *Flash Points of Organic and Organometallic Compounds*, Stevenson, R. M., New York, Elsevier, 1987
19. Bretherick, L., *Chem. Eng. News*, 1988, **66**(50), 2
20. Hasegawa, K. *et al., J. Loss Prev. Process Ind.*, 1991, **4**(3) 176
21. Kohlbrand, H. T., *Plant/Oper. Progr.*, 1991, **10**(1), 52
22. Anon., *Jahresbericht*, 1991, 73
23. Kong, D. *et al., J. Haz. Mat.*, 2003, **102**(2-3), 155

Flash point is defined as the minimum temperature at which a flammable liquid or volatile solid gives off sufficient vapour to form a flammable mixture with air.

There is usually a fair correlation between flash point and probability of involvement in fire if an ignition source is present in the vicinity of the source of the vapour; materials with low flash points being more likely to be involved than those with higher flash points. While no attempt has been made to include in this Handbook details of all known combustible materials, it has been thought worthwhile to include substances with flash points below 25°C, a likely maximum ambient temperature in many laboratories in warm temperate zones. These materials have been included to draw attention to the high probability of fire if such flammable or highly flammable materials are handled with insufficient care to prevent contact with of their vapours with an ignition source (stirrer motor, hot-plate, energy controller, flame, etc.). The figures for flash points quoted in Appendix 2 are closed cup values except where indicated by (o), and most are reproduced by permission of the two Companies concerned. A comprehensive listing of flash points for commercial liquids and formulated mixtures is also available [3,4]. A method for estimating approximate flash point temperatures based upon the boiling point and molecular structure was published. This involved calculation of the stoicheiometric concentration in air, followed by reference to a nomograph to give the flash point to within 11°C [5]. Many alternative methods of achieving the same ends have now been published, including one for hydrocarbons and alcohols [6], for mixtures of flammable and non-flammable liquids [7], and for partially miscible liquids (when activity coefficients must be known) [8]. Methods based on relative boiling points [9], or using a flame ionisation detector [10] have been described, and equations for use with multicomponent systems [11], or an additive group contribution method [12] are available among others [13,14]. Although chlorinated solvents are sometimes added to hydrocarbon solvents to raise the flash point, addition of inhibitor-containing 1,1,1-trichloroethane to a petroleum solvent actually reduced the flash point. This was attributed to the effect of the inhibitor [15], but this halogenated solvent, which has no flash point, will in fact burn and other haloalkanes have been shown to catalyse combustion.

The commonly accepted fallacy that liquids at temperatures below their flash points cannot give rise to flammable mixtures in air is dispelled with some examples of process operations with solvents at sub-atmospheric pressures. Under such conditions, flammable atmospheres may be generated at temperatures below the 1 Bar flash point. Conversely, flash points usually rise with increasing pressure. Thus, the real criterion should be whether flammable atmospheres can exist under given process conditions, rather than a flammable liquid being at a temperature below its flash point [16]. The use of a BASIC microcomputer program to calculate the flash points of organic compounds is described, based on the MW and functional groups present, and constants are given for 20 functional groups. Calculated values are satisfactory for monofunctional compounds, but not always for multifunctional compounds [17]. A new 296 page compilation of flash points is available [18]. There are a few halogenated hydrocarbons for which a flash point cannot be determined by standard tests, and these unfortunately are often described as non-flammable, though they will burn if the ignition source is sufficiently intense. Bromomethane, dichloromethane, trichloroethylene and 1,1,1-trichloroethane are compounds of this type [19].

The Japanese have started to measure the temperature corresponding to a composition of the upper explosive limit of a vapour in air under the name: Upper Flash Point. Some examples are given [20].

Liquids can form explosive atmospheres at temperatures below the flash point appropriate to the pressure in question if agitation is sufficient to form a mist. A destructive instance is reported [21].

Explosion of a reactor consequent upon taking a flash point (which refers to air) as indicating safety limits in pure oxygen is reported [22]. However, measurement of flashpoints with an enclosed apparatus generally showed little change in flash point with increasing oxygen concentration [23].

See FLAMMABILITY
See also MISTS

FLASH POWDER

1. Partington, 1967, 364
2. Bentzinger, von R. *et al., Praxis Naturwiss., Chem.*, 1987, **36**, 38
3. Young, J. A., *CHAS Notes*, 1991, **IX**(6), 2

Small portions of mixtures of magnesium powder with aluminium powder, with various oxidants (barium peroxide, barium nitrate, potassium chlorate, or even dry silica powder) were formerly used for flash photography [1]. During a classroom demonstration, several attempts were necessary before a large amount (20 g) of an old sample of flash powder could be ignited, but when ignition eventually occurred, a 20 cm fireball was produced, which caused severe burns [2]. Larger (20 kg) portions of similar mixtures may ignite more easily, and unexpectedly, with serious blast effects [3].

See Barium peroxide: Metals
Magnesium: Silicon dioxide, 4685
Potassium chlorate: Metals, 4011

FLOUR

1. Bond, 1991, 48
2. Cardillo. P., *J. Loss Prev. Proc. Ind.*, 2000, **14**, 69

A common fuel for dust explosions, with the distinction of causing the first such event investigated and recorded (in 1795) [1]. The same incident is given in fuller translation, (together with many other unrelated historical explosions) [2].

See DUST EXPLOSION INCIDENTS

FLUORINATED COMPOUNDS RF

See Lithium tetrahydroaluminate: Fluoroamides
Sodium: Fluorinated compounds, or: Halocarbons (reference 6), 4790

FLUORINATED CYCLOPROPENYL METHYL ETHERS

The individual compounds are:

1-Chloro-3,3-difluoro-2-methoxycyclopropene, 1407
3,3-Difluoro-1,2-dimethoxycyclopropene, 1860
1,3,3-Trifluoro-2-methoxycyclopropene, 1410

Methanol, or Water

Smart, B. E., *J. Org. Chem.*, 1976, **41**, 2377—2378

There are hazards involved both during the preparation and after isolation of these materials. Addition of sodium methoxide powder to perfluoropropene in diglyme at — 60°C led to ignition in some cases, and the products, 1,3,3-trifluoro-2-methoxycyclopropene (very volatile and flammable), or 3,3-difluoro-1,2-dimethoxycyclopropene, react violently with water or methanol, as does 1-chloro-3,3-difluoro-2-methoxycyclopropane.

FLUORINATED ORGANOLITHIUM COMPOUNDS

Anon., *Jahresber.*, 1981, 79

An unspecified partially fluorinated unsaturated ether was converted to the lithium salt with methyllithium in ether. A 70 g preparation exploded violently towards the end of the preparation, possibly owing to ingress of air down the stirrer guide when vacuum was applied to the flask. The hazardous nature of such compounds is stressed.

See Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide

2-, 3- or 4-Trifluoromethylphenylmagnesium bromide., 2639

Pentafluorophenyllithium, 2052

See Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS, ORGANOLITHIUM REAGENTS

FLUORINATED PEROXIDES AND SALTS $HOC(CF_3)_2OOM, F_5SOO—$

Anderson, L. R. *et al., J. Fluorine Chem.*, 1976, **7**, 481—500

Five derivatives, including the *O*—O lithium or sodium salts of the hydrogen peroxide adduct of hexafluoroacetone (2-hydroxyhexafluoro-2-propyl hydroperoxide), and their reaction products with acyl halides, are less flammable or explosive than their hydrocarbon analogues, though less stable than the parent hydroperoxides. Relevant entries are:

∗ Pentafluorosulfur peroxyacetate, 0752

∗ Pentafluorosulfur peroxyhypochlorite, : Haloalkenes, 3984

FLUORINATION

1. Grakauskas, V., *J. Org. Chem.*, 1970, **35**, 723; 1969, **34**, 2835
2. Sharts, C. M. *et al., Org. React.*, 1974, **21**, 125—265
3. Brekhovskikh, M. N. *et al., Mater. Res. Bull.*, 1988, **23**, 1417—1421

Safety precautions applicable to direct liquid phase fluorination of aromatic compounds are discussed [1]. Attention is drawn to the hazards attached to the use of many newer fluorinating agents [2]. In a study of fluorination reactions of hafnium and zirconium oxides by the fluoroxidisers xenon difluoride, chlorine trifluoride and bromine trifluoride, reactivity decreased in the order given [3].

See Fluorine

See ∗Pentafluorosulfur peroxyacetate,

See related UNIT PROCESS OR OPERATION INCIDENTS

FLUOROCARBONS C_nF_{2n+2}

Hydrogen (or methane)

1. Russian Institute for Fire Protection, *Chem. Abs.*, 2000, **132**, 209725
2. Editor’s suspicions

A variety of highly fluorinated compounds, retaining one functional group, hydrogen, other halogen or olefin, were tested as explosion inhibitors for mixtures of the combustible gases and air. The energy and rate of the subsequent explosions increased substantially [1]. Other studies have sometimes shown reductions in ignition energy. Thermodynamic calculations show considerable potential energy available from reaction of perfluoroalkyl moieties with hydrogen, less with methane. Such mixtures should not be considered inert [2]. Oxygen does nothing to improve them (see below).

Organometallic compounds

Fluorocarbon solvents are becoming widely used and the editor starts to encounter reports of low valency, or very highly basic, metal compounds exploding or incandescing on contact with them. Thermodynamically, formation of a metal-fluorine bond at the expense of a carbon-fluorine bond is always favourable, so metal/fluorocarbon pyrotechnic mixes find use as infra-red flares. Most experienced chemists must have noticed how Teflon equipment goes black when employed with alkali metal/amine reagents — that is surface reaction and formation of a protective carbon surface. Given any miscibility of metal reagent and fluorocarbon — which organic groups impart — there is no such protection, nor can liquid fluorocarbons thus shield themselves.

See 1-*tert*-Butyl-3-(*N*-*tert*-butyl-2-lithaminoethyl)imidazol-2-ylidene

See Sodium tris(η^4 naphthalene)tantalate(1-)

See also METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

Oxygen

1. Dawe, B. *et al., Chem. Eng. News*, 1991, **69**(23), 2
2. Taylor, J. E., *ibid.*, **69**(38), 2
3. Larsen, E. R., *ibid.*, 1992, **70**(7), 2
4. Christe, K. O., *ibid.*, 1991, **69**(40), 2

A liquid perfluorocarbon was being used as solvent in an oxidation by oxygen under pressure; more energy was released than expected [1]. It is cautioned that fluorocarbons are not inert to oxidation, presumably to carbonyl fluoride. An explosion has been experienced with perfluorotoluene in like circumstances [2]. A correspondent reports that perfluorotoluene is flammable in air, more saturated perfluorocarbons in pure oxygen [3]. Another detailed the combustion performance of polytetrafluoroethylene: 148 kcal/mole; ignition temperature not below 465°C at 7000 psi of oxygen [4], the product is mostly carbonyl fluoride. Other oxidants may also present a risk in extreme circumstances.

See Oxygen: Polymers
    Oxygen: Polytetrafluoroethylene, Stainless steel, 4825
    Poly(tetrafluoroethylene): Oxygen, 0625

FLUORODINITRO COMPOUNDS $FC(NO_2)_2$—, $FCH_2C(NO_2)_2$—

1. Peters, H. M. *et al., J. Chem. Eng. Data*, 1975, **20**(1), 113—117
2. Snaeberger, D. F., *Rept. UCID-16141*, Lawrence Livermore Lab., Univ. Calif., 1972

Several fluorodinitro compounds of methane (1,1,1-) and ethane (1,2,2-) are described as explosive, sensitive to initiation by impact, shock, friction or other means [1]. Procedures for safe handling of fluorine and explosive fluoronitro compounds are detailed [2].

FLUORODINITROMETHYL COMPOUNDS

1. Kamlet, M. J. *et al., J. Org. Chem.*, 1968, **33**, 3073
2. Witucki, E. F. *et al., J. Org. Chem.*, 1972, **37**, 152
3. Adolph, H. J., *J. Org. Chem.*, 1972, **37**, 749
4. Gilligan, W. H., *J. Org. Chem.*, 1972, **37**, 3947
5. Coon, C. L. *et al., Synthesis*, 1973, (10), 605—607
6. Gilligan, W. H. *et al., J. Chem. Eng. Data*, 1982, **27**, 94—99

Several of this group are explosives of moderate to considerable sensitivity to impact or friction and need careful handling. Fluorodinitromethane and fluorodinitroethanol are also vesicant [1]—[4]. 1-Fluoro-1,1-dinitro derivatives of ethane, butane, 2-butene and 2-phenylethane are explosive [5]. Among the preparations of a series of energetic and explosive compounds, that of *N,N,N′*,N′-tetrakis(2-fluoro-2,2-dinitroethyl)oxamide is especially hazardous, as it involves heating an undiluted explosive to a high temperature [6].

Individually indexed compounds are:
  Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane, 2415
  Bis(2-fluoro-2,2-dinitroethyl)amine, 1455
  2,2-Dinitro-2-fluoroethoxycarbonyl chloride, 1069
  1-Fluoro-1,1-dinitro-2-phenylethane, 2928
  1-Fluoro-1,1-dinitrobutane, 1557
  * 2(?)-Fluoro-1,1-dinitroethane, 0746
  1-Fluoro-1,1-dinitroethane, 0745
  2-Fluoro-2,2-dinitroethanol, 0747
  2-Fluoro-2,2-dinitroethylamine, 0796
  4-Fluoro-4,4-dinitrobutene, 1454
  Fluorodinitromethane, 0373
  Fluorodinitromethyl azide, 0340

See also ENERGETIC COMPOUNDS

FOAM BLANKETING FOR SPILL CONTROL

1. DiMaio, L. R. *et al., Plant/Oper. Progr.*, 1988, **7**, 195—198
2. Norman, E. C., *Vapour suppression by aqueous foams*, Chapter 2 in *Hazardous and toxic materials*, Fawcett, H. H. (ed.), New York, Wiley, 2nd edn., 1988

The use of aqueous foams to control fume or vapour release from reactive chemicals is discussed. An acid-resistant foam NF2 controlled fume emission from 35% and 65% oleum, and from titanium tetrachloride, but was not effective for sulfur trioxide and chlorosulfuric acid. An alcohol-resistant foam NF1 suppressed ammonia vapour emission by 80%, and Universal fire foam reduced evaporation of ethylene oxide, vinyl chloride and methanethiol, and reduced vapour emission of 1,3-butadiene by 60%. Safety aspects of foam blanketing are discussed [1]. Equipment and application techniques are covered in some detail [2].

FOAM RUBBER

1. Woolley, W. D. *et al., BRE CP 36/75*, Garston, Building Res. Est., 1975

2. Smith, E. E., *Consum. Prod. Flammability*, 1975, **2**, 589—69

A fire involving foam rubber mattresses in a storeroom led to an unexpected and serious explosion. Subsequent investigation showed that an explosion risk may exist when the flammable smoke and vapour from smouldering of large amounts of foam rubber are confined in an enclosed space. Suitable strict precautions are recommended [1]. Methods of quantitatively evaluating potential fire hazards from release rates of heat, smoke and toxic gases from heated foam rubber and plastics materials were developed, and their application to real situations discussed [2]. Autoignition of isocyanate foams made without proper temperature control during polymerisation is a known hazard [Ed.].

See also ORGANIC ISOCYANATES

Oxygen

See Oxygen (Gas): Polymers

FREEZE DRYING

See Sodium azide: Heavy metals (references 4,5)

FRICTIONAL IGNITION OF GASES AND VAPOURS

1. Powell, F., *Ind. Eng. Chem.*, 1969, **61**(12), 29
2. Desy, D. H. *et al., Rept. RI 8005*, Washington, US Bur. Mines, 1975
3. Uchida, S. *et al., Chem. Abs.*, 1984, **101**, 154290
4. van Laar, G. F. M., *EuropEx Newsl.*, 1986, (2), 9
5. Ihara, H. *et al., Chem. Abs.*, 1987, **107**, 80558
6. Krasnayanskii, M. M. *et al., Chem. Abs.*, 1987, **107**, 204305
7. Bartknecht, J., *Plant/Oper. Progr.*, 1988, **7**(2), 114—121.

The ignition of flammable gases and vapours by sparks from friction or impact was reviewed [1]. Ignition of methane by frictional impact of aluminium alloys and rusted steel has been investigated [2]. The effect of presence of beryllium in light alloys on the ignition of methane by sparks derived from their impact with rusted or corroded steel has been studied in a mining context [3]. Initiation of gases by mechanically derived sparks is discussed, including relationships between ignition sensitivity and minimum ignition temperatures and energies [4]. Ignition of methane by sparks produced by continuous contact of various metals with a rotating disc of the same or another metal has been studied [5]. From a study of a wide range of flammable organic vapours and gases by frictional sparks, it was concluded that only mixtures containing acetylene, carbon disulfide, carbon monoxide, hydrogen or methane could be so ignited. However, this conclusion is stated to be irrelevant if the temperature of the frictional surfaces exceeds the autoignition temperatures of the mixtures, or reaches 50—70°C [6]. The ignition capability of mechanically generated sparks or hot surfaces for gas and dust—air mixtures have been studied experimentally. A previous analysis of 357 industrial dust explosions had concluded that 30% were caused by mechanical sparks, and 5% by hot surfaces, but the results of this work show that the converse is likely to be true [7].

See FRICTIONAL INITIATION OF DUST CLOUDS, IGNITION SOURCES, THERMITE REACTIONS

FRICTIONAL INITIATION INCIDENTS

1. Cartwright, R. V., *Chem. Eng. News*, 1983, **61**(6), 4
2. Négyesi, G., *Process Safety Progress*, 1996, **15**(1), 42
3. Négyesi, G., *Process Safety Progress*, 1997, **16**(4), 237

Following the explosion of a perchlorate salt during filtration on a sintered funnel which caused severe injuries, the advantages of using plastic sintered funnels were stressed. Frictional heating will be much less on plastic sinters, and if explosive decomposition is initiated on a plastic funnel, fragmentation and resulting injuries should be much less with, for example, high-density polythene. (If the use of perchlorate salts cannot be avoided, fully appropriate measures for personal protection in addition to the use of plastic sinters seem essential [1].) Many non-explosive organic compounds, usually containing N or S heteroatoms, show decomposition, charring or sparks when subjected to friction or, less often, impact tests. This may be important as a source of ignition during grinding. Of 167 compounds tested, mostly pharmaceuticals and intermediates, 36 (listed) showed friction sensitivity. Testing of suspect compounds prior to industrial milling is suggested, with inerting or explosion protection measures for those proving positive [2]. Investigation of friction sensitivity of various pharmaceutical intermediates suggested that nitrogen-heterocycle carbothionamides may be sensitive to frictional ignition, apparently because of decomposition to give carbon disulphide and hydrogen sulphide, which have very low auto-ignition temperatures [3]. Other instances of frictional initiation are indexed under:

Barium : Halocarbons, 0200
Barium peroxide, 0216
1,2-Bis(azidocarbonyl)cyclopropane, 1829
* Calcium hypochlorite, 3918
Chromium trioxide : Potassium hexacyanoferrate(3—), 4236
Diazidodimethylsilane, 0914
Diazoacetonitrile, 0671
* Dimercury dicyanide oxide, 0979
Dimethylketene, 1515
Dysprosium perchlorate, 4125
Erbium perchlorate, 4126
Hexaamminechromium(III) perchlorate, 4123
† Phosphorus, 4868
Potassium chlorate : Metal phosphinates, 4011
Potassium perchlorate, 4012
Sodium 5-azidotetrazolide, 0548
Sodium chlorate : Paper, Static electricity, 4033
Sodium chlorate : Wood, 4033
Succinoyl diazide, 1434
Tetrakis(chloroethynyl)silane, 2874
Thianthrenium perchlorate, 3449

Triferrocenylcyclopropenium perchlorate, 3879
See other IGNITION SOURCES

FRICTIONAL INITIATION OF DUST CLOUDS

1. Pederson, G. H. *et al., Arch. Combust.*, 1987, **7**(1—2), 59—83
2. Dahn, C. J. *et al., ASTM Spec. Tech. Publ. 958*, (Ind. Dust Explos.), 1987, 324—332

At net impact energies below 20 J (approach velocities of 10—25 m/s), the heat generated by single impacts between various steels, between steel and rusty steel or concrete was insufficient to ignite dust clouds of corn starch, grain, feedstuffs or flour, even if dry. Dry dusts of titanium or zirconium may ignite, but not if 10% moisture is present in the cloud. Turbulence from a moving object in a dust cloud reduced the ignitability in the vicinity of the object. Impacts against a coarse surface (gravel) produced more sparking than against a smooth (cement-covered concrete) surface [1]. Six alloys, 2 of aluminium, a mild steel and 3 stainless were assessed for their ability to produce frictional sparks and to ignite dust clouds of various propellants and corn starch. The aluminium alloys showed the least hazard potential, and the ferrous alloys a greater tendency to cause ignition, particularly above frictional speeds of 9.2 m/s, and especially for long contact times [2].
See also FRICTIONAL IGNITION OF GASES AND VAPOURS

FRICTION DUST

Unpublished information, 1979
This is used in manufacture of brake linings and is a polymer based on cashew nutshell liquid admixed with formaldehyde or furfuraldehyde and other ingredients. The polymerised resin mixture is cast into 8 cm thick slabs and then ground finely to produce the friction dust. Several fires have been experienced during bulk storage of the dust, attributed to autoxidation of the still partially unsaturated resin compound. Previously, linseed oil was used in place of the nutshell liquid, but fires were then more frequent.

FULLER'S EARTH

Turpentine
See TURPENTINE: Diatomaceous earth

FULMINATING GOLD

Ephraim, 1939, 462—463
This appears not to be one specific compound or mixture, but is of variable composition, depending on the method of preparation. Prepared from gold chloride and aqueous ammonia, the explosive precipitate is largely $(ClAuNH_2)_2NH$, but on washing with ammonia hydrolysis to the more explosive $(HOAuNH_2)_2NH$ occurs, and the equilibrium is reversed by washing with chloride.
See Gold(III) chloride (and the entries following).

FULMINATING METALS

1. Tan, K. G., *Can. Inst. Metals Bull.*, 1987, **80**(903), 96—97
2. Bretherick, L., *Chem. Haz. Ind.*, 1988, (8), item 1595
3. Wilhelm, S. M., *Plant/Oper. Progr.*, 1991, **10**(4), 192

The fallacy that the ‘fulminating silver’ and ‘fulminating gold’ produced by reaction of ammonia with silver or gold salts are silver fulminate or gold fulminate is perpetuated in a comparatively recent publication [1]. In fact, ‘fulminating silver’ is largely silver nitride, Ag_3N, and ‘fulminating gold’, while of less certain constitution, contains several Au—N bonds. In contrast, the true fulminates, salts of hydrogen cyanide *N*-oxide, contain C—metal bonds [2].

Although the description ‘fulminating’ is not used and thus confusion with the fulminate not caused, mercury also forms explosive compounds of similar nature. The nitride (*ibid.*) is the most common and can be formed from the metal and ammonia in some circumstances, causing accidents where mercury manometers are used with ammonia. Halo- hydroxy- and oxy-nitrides can also be involved [3].

See GOLD COMPOUNDS, N-METAL DERIVATIVES, METAL FULMINATES, PRECIOUS METAL DERIVATIVES, SILVER COMPOUNDS

FULMINATING SILVER

Ephraim, 1939, 462

Fulminating silver is the most violently explosive compound among the nitrogen derivatives of the noble metals. Formed from action of ammonia on silver oxide, or on addition of potassium hydroxide to an ammoniacal solution of a silver salt, it is a black powder which explodes violently in the liquid in which it is formed if the slightest stirring is used. It probably contains amminesilver hydroxides, $[Ag(NH_3)_x]OH$.

See Silver chloride: Ammonia
Silver nitrate: Ammonia (4 items), 0022

FUME HOODS

Vogel, 5th Edn., 1989, p42

It is recommended that experiments with explosive chemicals not be conducted in the confinement of standard fume cupboards, with shatterable front and side panels, but on the open bench behind anchored polycarbonate blast screens. Even light top cover is found much to increase lateral blast effects. Specially designed laboratories are, of course, much preferable for such experiments.

Perchloric acid

See Perchloric acid: Fume cupboards

FUMES

1. Smith-Hansen, L. *et al., J. Loss Prevention*, 1993, **6**(4), 227; *ibid.*, 1995, **8**(2), 127
2. Christiansen, V., *J. Loss Prevention*, 1994, **7**(1), 39
3. Smith-Hansen, L., *Risoe Natl. Lab., [Rep] Risoe-R*, 1994; *Chem. Abs.*, 1995, **122**, 247076u

4. Smith-Hansen, L. *et al., Risoe Natl. Lab., [Rep] Risoe-R*, 1995; *Chem. Abs.*, 1996, **124**, 65180g
5. Orvis, A. *et al., Fire Mater.* '99, 6th Int. Conf., 1999, 95
6. Ruokojarvi, P. *et al., Chemosphere*, 2000, **41**(6), 825
7. Hietaniemi, J. *et al., Fire Mater.* 1999, 23(4), 149 & 171
8. Nelson, G. L., *Chem. Abs.*, 2001, **134**, 299816c
9. Lunghi, A. et al., J. Haz. Mat., 2004, 116(1-2), 11

Readers have indicated that they regard information on toxic fumes emitted in fires as important. This is not a simple subject and little is definitely known. Other reference works are packed with improbable products of 'heating to decomposition' (which is seldom distinguished from combustion). These appear to be the product of simplistic extrapolations from the empirical formulae. They also commonly list species which can have no existence under any conditions the human frame can tolerate, although they may, indeed, be present at 1000°C. What little experimental study has been reported indicates that in reality, as one would expect, the off-gases depend greatly on the fire conditions. Some Scandinavian studies have looked at pesticides, which contain an unusual wealth of hetero-atoms. There are always fumes of water, carbon monoxide and carbon dioxide. Nitrogen may appear as the element, as ammonia, as hydrogen cyanide, cyanic acid or as NO_x; sulphur as the element, as hydrogen sulphide and as sulphur dioxide. Phosphorus will emerge mostly as the pentoxide, (which will have picked up water before it gets near the lungs) and may possibly sometimes appear as phosphine. Chlorine usually appears as hydrogen chloride, but partially as the element and sometimes as phosgene. Bromine and iodine are more likely to appear as the element. Most of these materials seldom reach the levels of a 30 minute LC_{50} [1,2,3,4]. More recently, there has been much literature on the subject of poisonous fumes from fires but almost entirely directed at constructional materials. A few examples are given here: Infra-red techniques for identification of toxic fumes are reported, with reference to marine constructional materials [5]. House fires produce significant supposedly carcinogenic fumes (polycyclic aromatics, polychlorodibenzodioxins), which are deposited with the soot. Protective measures for fire-fighters are suggested [6]. [This is normal behaviour for all fires involving carbonaceous fuels and even traces of chlorides, e.g. driftwood bonfires on the beach – Ed.]. Of more direct 'chemical' import are further Scandinavian papers covering study of fumes and the influence of water spray upon them [7]. A conference paper has been given, looking at fire fatalities due to carbon monoxide, and considering what differences might be introduced with toxic-chemical fires [8]. As a consequence of the new European requirement to identify materials evolved in loss of containment accidents, a study of various organic chemicals, pyrolysed under conditions approximating to fire, attempts to relate structure to byproducts. The unquantified results differ little from the views above, some partial decomposition products, such as chlorobenzene and chlorobenzaldehyde, are also found but only from chloroaromatics [9].

Genuine acute dangers appear to be heat (the lungs cannot take air much above 60°C), oxygen depletion and carbon monoxide. These are found in all fires, even those involving no "chemicals" as the environmentalist considers them. A conference paper has been given, looking at fire fatalities due to carbon monoxide poisoning and considering what differences might be introduced with toxic chemical fires [8]. The obstruction to the lungs' function caused by deposition of solid carbon particles (soot) is also not chemical but none the less deleterious for that. Sulphur dioxide and hydrogen chloride (both readily detected irritants) may reach dangerous levels; hydrogen cyanide probably never does (except under conditions where CO is the greater danger) and nitrogen oxides only when the NO bond was already present in the starting material. Some NOx, the product of heating air, is always formed by hot fires anyway. Certain materials, such as fats, may produce irritant, if not actually toxic, fumes of propenal but poisonous organic fumes seem rare. However, pyrolysis is an excellent way of producing high energy species such as may induce chronic effects by interaction with nucleic acids, whether the starting material be tobacco, cannabis, dried banana-skin or whatever. It is not healthy to inhale more smoke than can be helped.

Readers are warned that the literature includes some incident reports originating from the emergency services which are undoubtedly in error. An example is the claimed production of hydrogen cyanide by fuels containing no nitrogen, but much chlorine (the ordinary gas detection tubes for cyanide actually generate and then measure hydrogen chloride; for which they have very limited absorption capacity in the pre-layer).

Since the European Seveso II Directive demands that industry discover what it may inadvertently produce and then emit when accidents happen, studies are starting on pyrolysis fumes, in an attempt to link these to functional groups [9]. The same group is also studying off-gases from other runaway reactions.

See also ENVIRONMENTALISM

FURAZAN N-OXIDES

1. Barnes, J. F. *et al., J. Chem. Soc., Perkin Trans.*, 1983, 294—295
2. Barnes, J. F. *et al., J. Chem. Soc., Chem. Comm.*, 1978, 113—114
3. Naixing, W. *et al., Propellants, Explos., Pyrotech.*, 1994, **19**(3), 145

Low MW strained-ring furazan *N*-oxides (furoxans) and some of their precursors are highly energetic compounds and should be handled carefully with due caution [1], and preferably in solution [2]. Benzofuroxans are reviewed, especially in relation to their explosive properties, which may be superior to corresponding nitrocompounds in energy, speed of detonation and bulk density [3]. Individually indexed compounds are:

4-(2′-Ammonio-2′-carboxyethylthio)-5,7-dinitro-4,5-dihydrobenzofurazanide *N*-oxide, 3140

Benzotri(furazan *N*-oxide), 2627

3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2626

4,5-Cyclopentanofurazan-*N*-oxide, 1865

Dicyanofurazan *N*-oxide, 1798

4,6-Dinitrobenzofurazan *N*-oxide, 2082

* 3-Ethyl-4-hydroxy-1,2,5-oxadiazole, 1500

4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2350

Potassium 3-methylfurazan-4-carboxylate 2-oxide, 1411

Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2107

Potassium 4-hydroxyamino-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2169

4a,5,7a,8-Tetrahydro-4,8-methano-4*H*-indeno[5,6-*c*]-1,2,5-oxadiazole 1- and 3-oxide, 3275

See other N-OXIDES

GAS CYLINDERS

1. *The Safe Filling, Handling, Storage and Distribution of Gases in Transportable Containers*, Code of Practice CP9, London, Brit. Comp. Gases Assoc., 1982
2. *Properties of Gases*, Wall Chart 57012, Poole, BDH Chemicals Ltd., 3rd edn., 1981
3. Braker, W. *et al., Matheson Gas Data Book*, E. Rutherford (NJ), Matheson Gas Products, 6th edn., 1981
4. *Guide to Safe Handling of Compressed Gases*, Lyndhurst (NJ), Matheson, 1982
5. *Handbook of compressed gases*, Compressed Gas Association Inc., New York, Van Nostrand-Reinhold, 2nd ed., 1981

The *Code of Practice* covers UK legislation, containers, identification and marking, valves, handling and storage, transportation, emergency procedures and personnel training. Data sheets for 114 gases are included [1]. An inexpensive wall chart summarises the important properties of 116 gases and volatile liquids [2]. The *Gas Data Book* gives comprehensive details of handling techniques and cylinder equipment necessary for 120 gases [3], and the newer guide covers the design of gas systems, premises, cylinder handling and storage, and air-monitoring techniques for a range of gases [4]. Another volume covers all aspects of handling gases in gas, liquid and solid states [5].

GAS EVOLUTION INCIDENTS

1. Lubernau, J. O., *Health Phys.*, 1986, **51**(1), 147
2. Lambert, P. G. *et al., Chem. & Ind.*, 1987, 490—491
3. Carson, P. J. *et al., Loss Prev. Bull.*, 1992, (102), 15
4. Lambert, P. G. *et al., Chem. Eng. Progress*, 1992, **88**(10), 53

Several incidents of pressure build-up in sealed containers of solutions of radioactive materials are noted for the period 1906—1985. The cause is radiolysis of the solvent, usually water, with evolution of hydrogen [1]. A method for evaluating gas evolution hazards in batch processing has been described. Based upon the use of a corrosion-resistant thermal mass flowmeter in conjunction with normal laboratory glassware, the electrical output can be fed either to a recorder/integrator, or to a data-logger/computer system. To exemplify the method, the rates of evolution of hydrogen chloride during the addition of carbon tetrachloride to a cold mixture of benzene and aluminium chloride (to form trityl chloride) are shown diagrammatically [2]. A list of combinations which may evolve toxic gases is given [3].

Although gas evolution is usually endothermic in open systems, and seldom a problem on laboratory scale, industrial batch reactors combine relatively far smaller vents with lower rupture pressures. This can give dangers with even endothermic evolutions. Exothermic gas evolving reactions readily become uncontrollable. A further hazard is nucleation and heating of saturated and supersaturated gas solutions when crystallisation of products occurs; this is the cause of many reactions jumping from flasks even in the lab. Details of combined calorimetric and gas flow safety-evaluation procedures are given [4]. A danger unremarked by the authors, but present in one of several examples, is autocatalysis of a slow step of the reaction by a non-gaseous product.

Elsewhere in the text, a number of incidents have involved evolution of gas(es) arising from slow decomposition or hydrolysis in storage, progressive thermal decomposition, or from other miscellaneous reactions or processing faults. Individual incidents may be found under:

Aluminium chloride, : Water, 0062
Aluminium hydride, : Carbon dioxide, or Sodium hydrogen carbonate, 0070
Aluminium phosphide, : Mineral acids, 0083
Americium trichloride, 0090
2-Ammoniothiazole nitrate, 1190
Argon, : Liquid nitrogen, 0091
Azidoiodoiodonium hexafluoroantimonate, 4355
Benzenesulfinyl chloride, 2227
Benzenesulfonyl chloride, 2228
Benzyl bromide, : Molecular sieve, 2731
Benzyl chloride, : Catalytic impurities, 2734
Bis(2-cyanoethyl)amine, 2391
1,2-Bis(chloromethyl)benzene, 2941
Bis(trimethylsilyl) peroxomonosulfate, 2598
Borane—tetrahydrofuran, 0138
Butylmagnesium chloride, 1636
Calcium acetylide, : Methanol, 0582
Calcium chloride, 3917
Cerium, : Water, 3955
Chlorine, : Chlorinated pyridine, Iron powder, 4041
Chlorine, : Dichloro(methyl)arsine, 4041
2-Chloromethylthiophene, 1836
* 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2970
* 2-Chloro-*N*-hydroxyacetamidine, 0845
Chlorosulfuric acid, : Hydrocarbons, 3991
Chlorosulfuric acid, : Sulfuric acid, 3991
Chromic acid, 4223
Chromium(II) chloride, 4046
Cyclohexanone oxime, 2446
1,4-Dicyano-2-butene, 2304
Diethyl dicarbonate, 2438
Diethyl sulfate, : Iron, Water, 1704
(Difluoroamino)difluoroacetonitrile, : Hydrazine, 0626
Difluoroammonium hexafluoroarsenate, 0098
1,1-Difluorourea, 0397
Dihydroxymaleic acid, 1443
† Diketene, : Acids, or Bases, or Sodium acetate, 1437
† Dimethyl sulfoxide, : Sodium hydride, 0917

Oxalic acid, : Urea, 0721
Peroxyacetic acid, : Metal chlorides, 0833
Phosphorus tribromide, : Phenylpropanol, 0292
Phosphorus trichloride, : Water, 4147
Phosphoryl chloride, : Water, 4143
Potassium bromate, : Aluminium, Dinitrotoluene, 0255
Pyrimidine-2,4,5,6-(1*H*,3*H*)-tetrone, 1394
Pyruvic acid, 1147
Sodium carbonate, 0549
Sodium chlorate, : or Non-metals, or Sulfides, 4033
Sodium dihydrobis(2-methoxyethoxy)aluminate, 2570
Sodium hydride, : Water, 4438
Sodium hydrogen carbonate, : Carbon, Water, 0389
Sodium hypochlorite, : Sodium ethylenediaminetetracetate, Sodium hydroxide, 4031
Sodium tetrahydroborate, 0147
Sodium tetrahydroborate, : Dimethyl formamide, 0147
Sodium triammine, 4576
Sulfinyl bromide, 0273
Sulfinyl chloride, : Dimethylformamide, 4090
Sulfinyl chloride, : Tetrahydrofuran, 4090
† Sulfur, : Limonene, 4891
Terephthaloyl chloride, 2884
1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent, 2072
Tetrachloroethylene carbonate, : Tributylamine, 1039
Tetrachlorosilane, : Ethanol, Water, 4167
Titanium, : Water, 4913
2-Toluenediazonium bromide, 2732
Trichloroacetaldehyde oxime, 0694
Trichloroperoxyacetic acid, 0655
Trifluoromethanesulfonic acid, : Acyl chlorides, Aromatic hydrocarbons, 0374
Trimethylsulfonium chloride, 1299
Trimethylsulfoxonium bromide, 1295
Uronium nitrate, 0492
ALKYL NITRATES: Lewis acids
CYANIDES: Hypochlorites
DEVARDA’S ALLOY
DIAZONIUM TETRAHALOBORATES
NITROBENZALDEHYDES
NITROBENZYL COMPOUNDS
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION
SUGARS
See also ISOXAZOLES

GAS HANDLING

1. O'Hanlon, J. F. *et al., J. Vac. Sci. Technol. A*, 1988, **6**(3, part 1), 1226—1254
2. *Photovoltaic safety*, Proc. Amer. Inst. Phys. Conf., 1988, 166

The American Vacuum Society's recommended procedures for handling hazardous gases include consideration of pump types, pump fluids, system design, effluent control, and storage of gases used for etching and deposition work. Examples of processes discussed in detail are aluminium plasma etching; silicon nitride, tungsten silicide, boron phosphosilicate-glass, silicon and gallium arsenide deposition; and ion implantation [1]. The conference dealt with various aspects of safety in gas handling systems in photovoltaic production processes, including a practical evaluation of wet gas-scrubbing systems, and a review of controlled combustion or oxidation of waste process gas streams. Gases discussed include arsine, diborane, disilane, hydrogen, hydrogen selenide, hydrogen telluride, phosphine, silane, trimethylaluminium and trimethylgallium [2].

See also CHEMICAL VAPOUR DEPOSITION

GEL CHROMATOGRAPHY

Silver staining

Demer, F. R., *University of Arizona Lab. Safety Notes*, 1990, (Fall), 2

A report of an explosion when mixing an outmoded silver staining reagent involving ammonia which could, and evidently did, form fulminating silver. Use of more modern safe formulations is commended.

See FULMINATING SILVER

GEOMETRY OF VESSELS AND PIPEWORK

1. Phylaktou, H. *et al., J. Loss Prevention*, 1993, **6**(1), 15 & 21
2. Chatrathi, K. *et al., Process Safety Progr.*, 1996, **15**(4), 237
3. Singh, *Process Safety Environ. Protect.*, 1994, **72**(B4), 220

The geometry of a detonable or deflagrating charge has a strong influence upon its performance. Pressure rise on ignition of gas/air mixtures in pipework was studied. In general, departures from the straight and narrow accelerated pressure rise and, presumably, transition to detonation [1]. A study of deflagration to detonation transition in pipes, for gas/air and dust mixtures has subsequently been published [2]. Gas explosions in interconnected vessels generate much higher pressures in the second, due to 'pressure piling'. A mathematical technique for prediction of hazard is given [3].

See DEFLAGRATION TO DETONATION

See also DUST EXPLOSION INCIDENTS, VAPOUR CLOUD EXPLOSIONS

GLASS INCIDENTS

1. Craig, T., *New Scientist*, 1995, **145**(1968), 33

Toughened glass used in fume cupboard windows can occasionally shatter explosively when edge defects are present. Although a physical hazard, it is possible to imagine it triggered by a small chemical explosion, which could even amplify the hazards of flying fragments. Application of polyester film to the outside of such windows is recommended [1].

There are several incidents in the text where glass has been involved as a direct cause, either because of its chemical properties (alkalinity, corrosive attack), or its physical properties (actinic transparency, or mechanical limitations under stress). Some of these incidents may be found under the entries:

Acrylic acid, : Initiator, Water, 1145
Aluminium chloride, : Water, 0062
Barium peroxide, : Propane, 0216
1,3-Benzodithiolium perchlorate, 2673
1,1-Bis(fluorooxy)tetrafluoroethane, 0637
Borane—tetrahydrofuran, 0138
Boron tribromide, : Water, 0122
Bromine, : Aluminium, Dichloromethane, 0261
Bromine, : Tungsten, Tungsten trioxide, 0261
† 1,3-Butadiene, 1476
Calcium oxide, : Water, 3931
Chlorine trifluoride, : Refractory materials, 3975
Chromium trioxide, : Acetic acid, 4236
Copper(II) oxide, : Boron, 4275
Diazoacetonitrile, 0671
Dihydroxymaleic acid, 1443
Ethyl azide, 0868
Ethylmagnesium bromide, : Water, 0843
Formic acid, 0417
† Hydrogen cyanide, 0379
Hydrogen hexafluorophophosphate, : Borosilicate glass, 4354
Hydrogen peroxide, : Diethyl ether, 4471
Imidazoline-2,4-dithione, 1138
Lithium nitride, : Silicon tetrafluoride, 4681
Magnesium, : Metal oxides, 4685
Manganese trifluoride, 4329
† Methyl acrylate, 1526
Nitric acid, : Glassware, 4430
Oxalic acid, : Urea, 0721
† Pentaborane(9), : Pentacarbonyliron, Pyrex glass, 0188
† Pentaborane(9), : Reactive solvents, 0188
Potassium hydroxide, : Glass, 4422
Potassium—sodium alloy, : Fluoropolymers, 4641
† Propene, : Lithium nitrate, Sulfur dioxide, 1194
Propiolaldehyde, 1082
Silicon dioxide, : Hydrochloric acid, 4833
Sodium sulfide, : Glass, 4805
Sodium tetrahydroborate, 0147
Succinic anhydride, : Sodium hydroxide, 1439
Sulfuric acid, : Hydrofluoric acid, 4473

Trifluoromethyl hypofluorite, : Lithium, 0352
2,4,6-Trimethylpyrilium perchlorate, 2987
Trimethylsulfonium chloride, 1299
Trimethylsulfoxonium bromide, 1295
Urea hydrogen peroxidate, 0475

GOLD CATALYSTS

Cusumano, J. A., *Nature*, 1974, **247**, 456

Supported metal catalysts containing gold should never be prepared by impregnation of a support with solutions containing both gold and ammonia. Dried catalysts so prepared contain extremely sensitive gold—nitrogen compounds which may explode at a light touch.

See FULMINATING GOLD, GOLD COMPOUNDS

GOLD COMPOUNDS

Many gold compounds exhibit a tendency to decompose violently with separation of the metal. Individually indexed compounds are:

Bis(dihydroxygold)imide, 0114
Chloromercuriodiphenylgold, 3466
Cyclopentadienylgold(I), 1833
* 1,2-Diaminoethanebis(trimethylgold), 3099
Diethylgold bromide, 1666
Digold(I) ketenide, 0571
Dimethylgold selenocyanate, 1196
Gold(I) acetylide, 0570
Gold(I) cyanide, 0307
Gold(I) nitride—ammonia, 0117
Gold(III) chloride, 0111
Gold(III) hydroxide—ammonia, 0112
Gold(III) nitride trihydrate, 0118
Gold(III) oxide, 0115
Gold(III) sulfide, 0116
Phenylgold, 2214
Sodium triazidoaurate(?), 0113
Tetracyanooctaethyltetragold, 3808
* Tetramethylbis(trimethysilanoxy)digold, 3376
Tetramethyldigold diazide, 1733
Triethylphosphinegold nitrate, 2553

See also PLATINUM COMPOUNDS, SILVER COMPOUNDS

GRAPHITE OXIDE

Boehm, H. P. *et al., Z. Anorg. Chem.*, 1965, **335**, 74—79

The oxide (an intercalated laminar material) is thermally unstable and on rapid heating it will deflagrate at a temperature dependent on the method of preparation.

This temperature is lowered by the presence of impurities, and dried samples of iron(III) chloride-impregnated oxide explode on heating.
See related NON-METAL OXIDES

GRAVEL

Forell, B. *et al., Müll. Abfall*, 1998, **30**(5), 327
Falling gravel is found to be an especial risk of ignition in boreholes containing flammable atmospheres. Flint, and some other forms of silica, are, of course, mechanical igniters of some antiquity. This observation brings into question use of gravel as a surface covering near where spills may be expected in chemical plants.
See Silicon dioxide
See IGNITION SOURCES

GRIGNARD REAGENTS RMgX, ArMgX

1. Kharasch and Reinmuth, 1954
2. Bondarenko, V. G. *et al., Chem. Abs.*, 1975, **82**, 89690
3. Brogli, F. *et al., Runaway Reactions*, Paper 3/M, 4, 7, Rugby, IChE, 1981
4. *See entry* SELF-ACCELERATING REACTIONS
5. Eckert, T. S., *J. Chem. Educ.*, 1987, **64**(2), 179
6. Sharkey, J. J. *et al. J. Loss Preventionc*, 1994, **7**(5), 413.
7. Ende, D. *et al., Org. Process Res. Dev.*, 1999, **3**(5), 319
8. Patterson, R. T., *Chim. Oggi*, 2000, 18(5), 5
9. Editor's comment, 2001

Preparation of Grignard reagents is frequently beset by practical difficulties in establishing the reaction (i.e. is usually subject to an induction period). Improved equipment and control methods for safer preparations have been described [2]. Initiation of the Grignard reaction has been studied in a heat flow calorimeter [3]. Addition of part of a previous reaction mass usually effects a smooth initiation [4]. An improved preparation of Grignard reagents (e.g. phenylmagnesium bromide) is described which involves the flame drying of assembled glassware in presence of iodine and magnesium to activate the latter. Ether must be excluded from the vicinity during this procedure [5]! Vent sizing calculations are given for industrial Grignard reactions [6]. A procedure for monitoring safe start up of Grignard reactions by Fourier Transform Infra-Red Spectroscopy is given [7]. A review suggests that safety may be improved by using glycol ethers as solvents instead of the customary ether or tetrahydrofuran [8]. Outside academic literature it is fairly well known that nothing much above stoichiometric levels of ethers is required, they being a necessary part of the reagent, but not a necessary solvent, which may be an aromatic hydrocarbon [9]

It is reported that the residual (and activated) magnesium left after a Grignard reaction may be pyrophoric. This is not, in fact, the usual case when the reaction is performed under nitrogen. Very possibly a protective nitride coating has formed on the metal. No such protection could be formed by argon, increasingly used as inert gas blanket in academe. Grignard reagents themselves heat rapidly on exposure to atmospheric oxygen [9].

Individually indexed compounds are:

- * Bromomethane, : Metals, 0428
- Butylmagnesium chloride, 1636
- * Ethyl acetoacetate, : 2,2,2-Tris(bromomethyl)ethanol, Zinc, 2434
- Ethylmagnesium bromide, 0843
- Ethylmagnesium iodide, 0855
- Methylmagnesium iodide, 0445
- Phenylmagnesium bromide, 2218
- 4-Trifluoromethylphenylmagnesium bromide, 2639
- 3-Trifluoromethylphenylmagnesium bromide, 2639
- 2-Trifluoromethylphenylmagnesium bromide, 2639

See other HALO-ARYLMETALS
See related UNIT OPERATION OR PROCESS INCIDENTS

HALOACETYLENE DERIVATIVES —C≡CX

1. Whiting, M. C., *Chem. Eng. News*, 1972, **50**(23), 86
2. Brandsma, 1971, 99
3. Kloster-Jensen, E. *et al., Chem. Eng. News*, 1978, **56**(19), 38

The tendency towards explosive decomposition noted for dihalo-2,4-hexadiyne derivatives appears to be associated more with the co-existence of halo- and acetylene functions in the same molecule, than with its being a polyacetylene. Haloacetylenes should be used with exceptional precautions [1]. Explosions may occur during distillation of bromoacetylenes when bath temperatures are too high, or if air is admitted to a hot vacuum-distillation residue [2]. Precautions necessary in isolating and handling such compounds on the small (1 g) scale are detailed [3]. Individually indexed compounds are:

- 1-Bromo-1,2-cyclotridecadien-4,8,10-triyne, 3593
- Bromoacetylene, 0647
- Bromochloroacetylene, 0575
- † 3-Bromopropyne, 1087
- * Calcium hypochlorite, : Acetylene, 3918
- 3-Chloro-1-iodopropyne, 1070
- 4-Chloro-2-butynol, 1451
- 1-Chloro-3-phenylpent-1-en-4-yn-3-ol, 3387
- Chloroacetylene, 0648
- Chlorocyanoacetylene, 1033
- Chloroiodoacetylene, 0595
- † 3-Chloropropyne, 1089
- Copper(I) chloroacetylide, 1350
- * 3-Cyanopropyne, 1412
- 1,4-Dibromo-1,3-butadiyne, 1347
- Dibromoacetylene, 0579
- 1,4-Dichloro-1,3-butadiyne, 1349
- 1,6-Dichloro-2,4-hexadiyne, 2150
- 1,4-Dichloro-2-butyne, 1424

Dichloroacetylene, 0599
† Dicyanoacetylene, 1795
Difluoroacetylene, 0619
1,4-Diiodo-1,3-butadiyne, 1793
1,6-Diiodo-2,4-hexadiyne, 2166
Diiodoacetylene, 0981
Fluoroacetylene, 0658
1-Iodo-1,3-butadiyne, 1377
3-Iodo-1-phenylpropyne, 3114
1-Iodo-3-penten-1-yne, 1839
Iodoacetylene, 0666
3-Iodopropyne, 1102
* Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide, 1814
Lithium bromoacetylide, 0577
Lithium chloroacetylide, 0596
Lithium trifluoropropynide, 1043
Mercury bis(chloroacetylide), 1352
* Silver chloroacetylide, 0563
Silver trifluoropropynide, 1026
Sodium bromoacetylide, 0578
Sodium chloroacetylide, 0598
Tetrakis(chloroethynyl)silane, 2874
Thallium(I) iodacetylide, 0980
3,3,3-Trifluoropropyne, 1063

HALOALKANES RX

1. Bretherick, L., *Chem. & Ind.*, 1986, 729; *Chem. Eng. News*, 1986, **64**(51), 2
2. Suzuki, A. *et al., Bull. Chem. Soc. Jap.,* 1991, **64**(11), 3345

Of the lower members of this reactive group of compounds, the more lightly substituted are of high flammability like the haloalkenes. The more highly substituted find use as fire suppressants, not always with the anticipated results: Bromotrifluoromethane can promote ignition of mixtures of air and methane (but not ethane) [1]; up to 5% tetrafluoromethane accelerates detonation of hydrogen oxygen mixtures [2]. Reaction with the lighter divalent metals may give much more reactive materials analogous to Grignard reagents. Individually indexed compounds are:

* 1,4-Bis(1,2-dibromoethyl)benzene, 3262
* 1,3-Bis(trichloromethyl)benzene, 2886
* 1,3-Bis(trifluoromethyl)benzene, 2889
3-Bromo-1,1,1-trichloropropane, 1123
* 2-Bromo-2,5,5-trimethylcyclopentanone, 3013
† 1-Bromo-2-methylpropane, 1628
† 2-Bromo-2-methylpropane, 1629
† 1-Bromo-3-methylbutane, 1978
† 2-Bromobutane, 1627

† 1-Bromobutane, 1626
† Bromoethane, 0842
Bromoform, 0367
† Bromomethane, 0428
† 2-Bromopentane, 1979
† 1-Bromopropane, 1237
† 2-Bromopropane, 1238
Bromotrichloromethane, 0309
Bromotrifluoromethane, 0310
Carbon tetrabromide, 0314
Carbon tetrachloride, 0331
Carbon tetrafluoride, 0348
Carbon tetraiodide, 0522
† 1-Chloro-1,1-difluoroethane, 0727
† 2-Chloro-2-methylbutane, 1981
† 2-Chloro-2-methylpropane, 1635
† 1-Chloro-2-methylpropane, 1634
† 1-Chloro-3,3,3-trifluoropropane, 1124
† 1-Chloro-3-methylbutane, 1980
† 2-Chlorobutane, 1633
† 1-Chlorobutane, 1632
† Chlorocyclopentane, 1917
Chlorodifluoromethane, 0368
† Chloroethane, 0844
Chloroform, 0371
† Chloromethane, 0431
† Chloromethyl ethyl ether, 1242
† Chloromethyl methyl ether, 0846
† 1-Chloropentane, 1982
† 1-Chloropropane, 1239
† 2-Chloropropane, 1240
1,2-Dibromoethane, 0781
Dibromomethane, 0394
Dichlordifluoromethane, 0325
1,1-Dichloro-1-fluoroethane, 0734
2,2-Dichloro-3,3-dimethylbutane, 2463
† *mixo*-Dichlorobutane, 1582
† 1,1-Dichloroethane, 0786
† 1,2-Dichloroethane, 0787
† Dichloromethane, 0396
2,2-Dichloropropane, 1201
† 1,1-Dichloropropane, 1199
† 1,2-Dichloropropane, 1200
1,2-Dichlorotetrafluoroethane, 0601
† 1,1-Difluoroethane, 0797
Diiodomethane, 0399

Fluorodiiodomethane, 0372
† Fluoroethane, 0851
† Fluoromethane, 0440
Hexabromoethane, 0581
* 1,2,3,4,5,6-Hexachlorocyclohexane, 2299
Hexachloroethane, 0608
† 2-Iodo-2-methylpropane, 1644
† 1-Iodo-2-methylpropane, 1643
† 2-Iodobutane, 1642
Iodoethane, 0854
* 2-Iodoethanol, 0856
Iodoform, 0375
Iodomethane, 0444
† 2-Iodopentane, 1984
† 2-Iodopropane, 1248
Pentachloroethane, 0656
* Poly(carbon monofluoride), 0336
* Poly(chlorotrifluoroethylene), 0589
* Poly(tetrafluoroethylene), 0625
* Tetracarbon monofluoride, 1358
1,1,2,2-Tetrachloroethane, 0695
† 1,1,1-Trichloroethane, 0737
1,1,2-Trichloroethane, 0738
* 2,2,2-Trichloroethanol, 0741
Trichlorofluoromethane, 0329
1,1,2-Trichlorotrifluoroethane, 0603
† 1,1,1-Trifluoroethane, 0751

Azides

Nzeyimana E. *et al., Progr. Aeronaut. Astronaut.* 1991, (133), 77

Potential hazards arising from slow formation of explosive azides from prolonged contact of halogenated solvents with metallic or other azides are outlined.

HALOALKENES —C=CX

Of the lower members of this reactive group of compounds, the more lightly substituted are of high flammability and many are classed as peroxidisable and as polymerisable compounds. Individually indexed compounds are:

† Acrylonitrile, 1104
† 4-Bromo-1-butene, 1544
† 3-Bromo-1-propene, 1149
† 1-Bromo-2-butene, 1543
4-Bromocyclopentene, 1878
† Bromoethylene, 0723
† Bromotrifluoroethylene, 0576
† 2-Chloro-1,3-butadiene, 1447
† 3-Chloro-1-butene, 1547

† 1-Chloro-1-propene, 1152
† 2-Chloro-2-butene, 1546
† 3-Chloro-2-methyl-1-propene, 1548
† 2-Chloroacrylonitrile, 1071
3-Chlorocyclopentene, 1879
† Chloroethylene, 0726
† 2-Chloropropene, 1153
† 3-Chloropropene, 1154
† Chlorotrifluoroethylene, 0588
3,5-Dibromocyclopentene, 1854
* (2,2-Dichloro-1-fluorovinyl)ferrocene, 3463
† *trans*-1,2-Dichloroethylene, 0693
† 1,1-Dichloroethylene, 0691
† *cis*-1,2-Dichloroethylene, 0692
† 2,3-Dichloropropene, 1129
† 1,1-Difluoroethylene, 0696
* 2-Ethoxy-1-iodo-3-butene, 2443
† Fluoroethylene, 0744
Hexachlorocyclopentadiene, 1802
† Hexafluoropropene, 1048
1-Iodohexa-2,4-diene, 2387
† 3-Iodopropene, 1170
* Methyl trifluorovinyl ether, 1098
1,2,3,-5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2062
1,2,3,-4,5-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2062
Perfluorobutadiene, 1360
* Poly(1-pentafluorothio-1,2-butadiyne), 1375
1,1,2,3-Tetrachloro-1,3-butadiene, 1385
1,1,4,4-Tetrachlorobutatriene, 1356
Tetrachloroethylene, 0606
Tetrachloropropadiene, 1038
1,1,4,4-Tetrafluorobutatriene, 1359
† Tetrafluoroethylene, 0624
Tetraiodoethylene, 0982
† Trichloroethylene, 0652
† Trifluoroethylene, 0659
† 3,3,3-Trifluoropropene, 1096
See other PEROXIDISABLE COMPOUNDS

HALOANILINES $XC_6H_4NH_2$

Kotoyori, T., *Proc. 6th Int. Sympos. Loss Prev. Safety Prom, Proc. Ind.*, 38-1—38-16, Oslo, Norweg. Soc. Chartered Engrs., 1989

Available information on the thermal instability of halogenated anilines during vacuum distillation is presented and analysed, and the roles of dehyrohalogenation, polymerisation, salt formastion and dissociation, aerobic oxidation, corrosion and metal-catalysed decomposition are discussed. Experimental work on these topics is presented, and preventive measures proposed.

Some halo-substituted anilines are of limited thermal stability, tending to eliminate hydrogen halide which may catalyse further decomposition. To avoid decomposition during distillation, this should be conducted in the presence of solid alkali or magnesium oxide at minimum temperature (under relatively high vacuum) and/or with exclusion of air by inert gas. Individually indexed compounds are:

* 4-Bromo-1,2-diaminobenzene, 2338
2-Bromo-3,5-dimethoxyaniline, 2969
4-Bromoaniline, 2289
4-Bromodimethylaniline, 2968
* 4-Chloro-1,2-benzenediamine, 2340
* 4-Chloro-1,3-benzenediamine, 2341
2-Chloro-1,4-benzenediamine, 2342
4-Chloro-2,6-diamino-*N*-methylaniline, 2818
4-Chloro-2-aminophenol, 2296
4-Chloro-2-methylaniline, 2790
3-Chloro-4-methoxyaniline, 2791
4-Chloroaniline, 2295
3-Chloroaniline, 2294
2-Chloroaniline, 2293
* 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2970
2,4-Dibromoaniline, 2219
2,4-Dichloroaniline, 2231
2,5-Dichloroaniline, 2232
3,4-Dichloroaniline, 2234
2,3,4-Trichloroaniline, 2156

HALOARENEMETAL π-COMPLEXES $[(F_6C_6)_2M]$ etc.

1. Klabunde, K. *et al., Inorg. Chem.*, 1975, **14**, 790—791
2. Klabunde, K. *et al., Angew. Chem. (Intern. Ed.)*, 1975, **14**, 288
3. Klabunde, K. *et al., J. Fluorine Chem.*, 1974, **4**, 11
4. Graves, V. *et al., Inorg. Chem.*, 1976, **15**, 578

The π-complexes formed between chromium(0), vanadium(0) or other transition metals, and mono- or poly-fluorobenzene show extreme sensitivity to heat and are explosive [1,2]. Hexafluorobenzenenickel(0) exploded at 70°C [3], and presence of two or more fluorine substituents leads to unstable, very explosive chromium(0) complexes [1]. Apparently, the aryl fluorine atoms are quite labile, and on decomposition M—F bonds are formed very exothermically. Laboratory workers should be wary of such behaviour in any haloarenemetal π-complex of this type [1]. However, in later work, no indications of explosivity, or indeed of any complex formation, were seen [4]. Individually indexed compounds are:

Bis(1,n-difluorobenzene)chromium(0) isomers, 3455
Bis(fluorobenzene)chromium(0), 3470
Bis(fluorobenzene)vanadium(0), 3471

Bis(hexafluorobenzene)chromium(0), 3415
Bis(hexafluorobenzene)cobalt(0), 3413
Bis(hexafluorobenzene)iron(0), 3418
Bis(hexafluorobenzene)nickel(0), 3419
Bis(hexafluorobenzene)titanium(0), 3420
Bis(hexafluorobenzene)vanadium(0), 3421
See other HALO-ARYLMETALS

HALOARYL COMPOUNDS ArX

Though normally not very reactive, a few haloaryl compounds if sufficiently activated by other substituents or by specific reaction conditions, may undergo violent reactions. Individually indexed compounds are:

Bis(2,4,5-trichlorobenzenediazo) oxide, 3425
Bis(4-chlorobenzenediazo) oxide, 3450
* 1,3-Bis(trichloromethyl)benzene, 2886
* 1,3-Bis(trifluoromethyl)benzene, 2889
Bromobenzene, 2217
1-Chloro-2,4-dinitrobenzene, 2091
4-Chloro-2,5-diethoxynitrobenzene, 3295
4-Chloro-2-methylphenol, 2737
2-Chloro-5-nitrobenzenesulfonic acid, 2137
Chlorobenzene, 2221
† 2-Chlorofluorobenzene, 2127
† 3-Chlorofluorobenzene, 2128
† 4-Chlorofluorobenzene, 2129
2-Chloronitrobenzene, 2134
4-Chloronitrobenzene, 2135
4-Chlorotrifluoromethylbenzene, 2642
1,5-Dichloro-2,4-dinitrobenzene, 2070
1,2-Dichlorobenzene, 2149
3,4-Dichloronitrobenzene, 2098
2,4,-Dichloronitrobenzene, 2097
Dichlorophenol mixed isomers, 2154
1,5-Difluoro-2,4-dinitrobenzene, 2073
† 1,3-Difluorobenzene, 2161
† 1,4-Difluorobenzene, 2162
1,2-Diiodobenzene, 2165
* 1-Fluoro-2,4-dinitrobenzene, 2101
† Fluorobenzene, 2241
† 4-Fluorotoluene, 0027
† 2-Fluorotoluene, 0027
† 3-Fluorotoluene, 0027
2-Iodo-3,5-dinitrobiphenyl, 3444
Iodobenzene, 2242
4-Iodotoluene, 2746

1,2,4,5-Tetrachlorobenzene, 2072
† 1,2,4,5-Tetrafluorobenzene, 2074
2,4,5-Trichlorophenol, 2100
† 1,2,4-Trifluorobenzene, 2103

HALO-ARYLMETALS **ArMX, XArM**

The name adopted for this group of highly reactive (and in some circumstances intramolecularly self-reactive) compounds is intended to cover both arylmetal halides (halogen bonded to the metal) and haloaryl metals (halogen attached to the aryl nucleus). Individually indexed compounds are:

Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, 3824
* Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide, 3696
Bis(pentafluorophenyl)aluminium bromide, 3412
* Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel, 3831
3-Bromophenyllithium, 2122
4-Bromophenyllithium, 2123
4-Chlorophenyllithium, 2132
3-Chlorophenyllithium, 2131
4-Fluorophenyllithium, 2159
Pentafluorophenylaluminium dibromide, 2047
Pentafluorophenyllithium, 2052
Tetrakis(pentafluorophenyl)titanium, 3836
2-Trifluoromethylphenyllithium, 2651
3-Trifluoromethylphenyllithium, 2651
4-Trifluoromethylphenyllithium, 2651
4-Trifluoromethylphenylmagnesium bromide, 2639
2-Trifluoromethylphenylmagnesium bromide, 2639
3-Trifluoromethylphenylmagnesium bromide, 2639
HALOARENEMETAL π-COMPLEXES
ORGANOLITHIUM REAGENTS
See GRIGNARD REAGENTS

HALOBORANES **—BHX, —BX_2**

The degree of reactivity to air or to water depends on the degree of substitution of hydrogen by halogen. This highly reactive group includes the individually indexed compounds:

Bromodiborane, 0159
1-Bromopentaborane(9), 0186
Chlorodiborane, 0160
* *B*-Chlorodimethylaminodiborane, 0958
* *B*-Chlorodimethylaminodiborane, 0958
Diboron tetrachloride, 0161
Diboron tetrafluoride, 0162
1,2-Dibromopentaborane(9), 0187
Iododiborane, 0165

Tetraboron tetrachloride, 0179
See related NON-METAL HALIDES, NON-METAL HYDRIDES

HALOCARBONS **RX, ArX**

This generic name often to be found in the text is used in the sense of halogen-substituted hydrocarbons which may also contain hydrogen, i.e. substitution may not necessarily be complete. It represents a range of halogenated aliphatic or aromatic compounds widely used in research and industry, often as solvents or diluents. None are completely inert chemically, but in general, reactivity decreases with increasing substitution of hydrogen by halogen (particularly with fluorine), in both saturated and unsaturated hydrocarbons.

Several lower partially halogenated hydrocarbons (dichloromethane, bromomethane, trichloroethylene, 1,1,1-trichloroethane) have no measurable flash point, but are nonetheless capable of forming flammable and explosive mixtures with air, and several such accidents are recorded.

Calcium disilicide, : Carbon tetrachloride, 3938
Dinitrogen tetraoxide, : Halocarbons, 4720
Disilane, : Non-metal halides, 4564
Fluorine, : Halocarbons, 4304
Oxygen (Liquid), : Halocarbons, 4826
Pentaborane(9),: Reactive solvents, 0188
CHLOROFLUOROCARBONS
FLUOROCARBONS
HALOALKANES
HALOALKENES
HALOARYL COMPOUNDS
See METAL—HALOCARBON INCIDENTS
See entry FLASH POINTS (reference 19)

HALOGENATION INCIDENTS

Examples of incidents involving halogenation reactions are:

Bromine, : Alcohols, 0261
Bromine, : Aluminium, Dichloromethane, 0261
Bromine, : Isobutyrophenone, 0261
N-Bromosuccinimide, : Dibenzoyl peroxide, 4-Toluic acid, 1421
Chlorine, 4041
Chlorine, : 2-Chloroalkyl aryl sulfides, Lithium perchlorate, 4041
Chlorine, : Antimony trichloride, Tetramethylsilane, 4041
Sulfur tetrafluoride, : 2-(Hydroxymethyl)furan, Triethylamine, 4344
Titanium, : Halogens, 4913
Trifluoromethanesulfenyl chloride, : Chlorine fluorides, 0321
ALKYLALUMINIUM DERIVATIVES: Halocarbons
BORANES: Carbon tetrachloride
N-HALOIMIDES: Xylene
SILANES: Chloroform

See other UNIT PROCESS INCIDENTS

HALOGEN AZIDES XN_3

Metals, or Phosphorus

Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 240

A comprehensive review covers stability relationships and reactions of these explosive compounds and their derivatives. Bromine, chlorine and iodine azides all explode violently in contact with magnesium, zinc or white phosphorus.

Individually indexed compounds are:

Bromine azide, 0256
Chlorine azide, 4024
* Cyanogen azide, 0541
Fluorine azide, 4301
Iodine azide, 4616

See METAL PNICTIDES

See other N-HALOGEN COMPOUNDS, NON-METAL AZIDES

N-HALOGEN COMPOUNDS —NX

1. Kovacic, P. *et al., Chem. Rev.*, 1970, **70**, 640
2. Petry, R. C. *et al., J. Org. Chem.*, 1967, **32**, 4034
3. Freeman, J. P. *et al., J. Amer. Chem. Soc.*, 1969, **91**, 4778
4. Guillamin, J. C. *et al., Synthesis*, 1985, (12), 1131—1133
5. Guillamin, J. C. *et al.,Tetrahedron*, 1988, **44**, 4431—4446; 4447—4455
6. Kirk-Othmer, 1993, (4th Edn) Vol IV, 917, 921

Many compounds containing one or more N—X bonds show unstable or explosive properties (and are also oxidants), and this topic has been reviewed [1]. Difluoroamino compounds, ranging from difluoramine and tetrafluorohydrazine to polydifluoroamino compounds, are notably explosive and suitable precautions have been detailed [2,3]. Preparative scale *N*-chlorination of 1y and 2y amines by passing them over *N*-chlorosuccinimide is described. In presence of alumina, 1y amines give the *N,N*-dichloro derivatives. The products must be handled with great caution, and collection and storage at —30°C is recommended, as some of the products exploded at ambient temperature [4]. The range of compounds so prepared has been further extended [5]. *N*-Halosulfinylamines (O=S=NHal) are stable at room temperature but react explosively with water. Dialkyldichlorosulfurdiimides [$R2S(=NCl)_2$] explode violently when heated [6].

Within this class fall the separate groups:

Individually indexed compounds are:

Azidoiodoiodonium hexafluoroantimonate, 4355
Azo-*N*-chloroformamidine, 0788
Benzoquinone 1,4-bis(chloroimine), 2152
1,4-Benzoquinone-4-chloroimine, 2133
4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene, 1861
Bromamine, 0249
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2641

N-Bromo-3-nitrophthalimide, 2879
N-Bromoacetamide, 0780
1-Bromoaziridine, 0779
N-Bromosuccinimide, 1421
N-Bromotetramethylguanidine, 1996
N-Bromotrimethylammonium bromide(?), 1296
Chloramine, 3994
* Chloriminovanadium trichloride, 4159
N-Chloro-3-aminopropyne, 1126
N-Chloro-3-aminopropyne, 1126
N-Chloro-3-morpholinone, 1485
N-Chloro-4,5-dimethyltriazole, 1486
N-Chloro-4-methyl-2-imidazolinone, 1549
N-Chloro-4-nitroaniline, 2224
N-Chloro-5-methyl-2-oxazolidinone, 1484
N-Chloro-5-phenyltetrazole, 2670
N-Chloroacetamide, 0785
N-Chloroallylamine, 1198
1-Chloroaziridine, 0782
1-Chlorobenzotriazole, 2143
N-Chloro-bis(2-chloroethyl)amine, 1585
N-Chlorobis(trifluoromethanesulfonyl)imide, 0593
N-Chlorocinnamaldimine, 3120
N-Chlorodimethylamine, 0891
N-Chloropiperidine, 1942
N-Chloropyrrolidine, 1579
N-Chlorosuccinimide, 1423
N-Chlorotetramethylguanidine, 1998
Diamminedichloroamidotrichloroplatinum(IV), 4173
2,6-Dibromobenzoquinone-4-chloroimide, 2069
Dichloramine, 4057
1-Dichloroaminotetrazole, 0370
N,N-Dichloroaniline, 2235
2,6-Dichlorobenzoquinone-4-chloroimide, 2071
N,N’-dichlorobis(2,4,6-trichlorophenyl)urea, 3590
Dichlorofluoramine, 4053
N,N-Dichloroglycine, 0735
N,N-Dichloromethylamine, 0436
N,N-Dichloropentafluorosulfanylamine, 4054
N,N-Dichloro-β-alanine, 1164
Difluoramine, 4305
3-Difluoroamino-1,2,3-trifluorodiaziridine, 0357
* Difluoroammonium hexafluoroantimonate, 4374
Difluoroammonium hexafluoroarsenate, 0098
Difluorodiazene, 4308
Difluoro-*N*-fluoromethanimine, 0343

Diiodamine, 4420
Dimethyl *N,N*-dichlorophosphoramidate, 0897
1,1-Dimethylethyldibromamine, 1631
Ethyl *N*-chloro-*N*-sodiocarbamate, 1155
Fluoramine, 4290
3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine, 0627
1-Fluoroiminohexafluoropropane, 1055
2-Fluoroiminohexafluoropropane, 1056
N-Fluoroiminosulfur tetrafluoride, 4351
N-Fluoro-*N*-nitrobutylamine, 1640
* Iodine isocyanate, 0521
Nitrogen chloride difluoride, 3972
Nitrogen tribromide hexaammoniate, 0289
Nitrogen trichloride, 4137
Nitrogen trifluoride, 4330
Nitrogen triiodide—silver amide, 4629
Nitrogen triodide, 4628
Nitrogen triodide—ammonia, 4630
Nitrosyl chloride, 4017
Nitrosyl fluoride, 4296
Nitryl chloride, 4019
Nitryl fluoride, 4297
* Pentafluoroguanidine, 0358
Sodium *N*-chloro-4-toluenesulfonamide, 2735
Sodium *N*-chlorobenzenesulfonamide, 2222
N,N,N″,N″-Tetrachloroadipamide, 2363
Tetrafluoroammonium hexafluoromanganate, 4378
Tetrafluoroammonium hexafluoronickelate, 4379
Tetrafluoroammonium octafluoroxenate, 4380
Tetrafluoroammonium perbromate, 0242
Tetrafluoroammonium perchlorate, 3980
Tetrafluoroammonium tetrafluoroborate, 0133
Tetrafluorodiaziridine, 0350
† Tetrafluorohydrazine, 4339
Tetrakis(*N,N*-dichloroaminomethyl)methane, 1894
Tribromamine oxide, 0290
1,3,5-Trichloro-2,4,6-trifluoroborazine, 0173
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine, 4139
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum, 4136
Trifluoroacetyliminoiodobenzene, 2898
2,4,6-Tris(bromoamino)-1,3,5-triazine, 1088
2,4,6-Tris(dichloroamino)-1,3,5-triazine, 1040

N-CHLORONITROAMINES
DIFLUOROAMINO COMPOUNDS
HALOGEN AZIDES
N-HALOIMIDES

N—S COMPOUNDS
N,N,N′-TRIFLUOROALKYLAMIDINES

HALOGEN OXIDES XO_n

Of the various compounds arising from union of oxygen with one or more halogens, many are endothermic and all are generally unstable but powerful oxidants. Individually indexed compounds are:

Bromine bromate, 0275
Bromine dioxide, 0258
Bromine perchlorate, 0235
Bromine trioxide, 0259
Bromyl fluoride, 0239
Chlorine dioxide, 4036
Chlorine perchlorate, 4095
Chlorine trifluoride oxide, 3976
Chlorine trioxide, 4038
Chloryl hypofluorite, 3967
Chloryl perchlorate, 4098
Dichlorine oxide, 4089
Dichlorine trioxide, 4094
* Dicyanogen *N,N′*-dioxide, 0994
Dioxygen difluoride, 4314
Fluorine perchlorate, 3970
Hexaoxygen difluoride, 4321
Iodine dioxide trifluoride, 4328
Iodine(V) oxide, 4622
Iodine(VII) oxide, 4623
Oxygen difluoride, 4311
Perbromyl fluoride, 0240
Perchloryl fluoride, 3968
Perchloryl perchlorate, 4101
Tetrafluoroiodosyl hypofluorite, 4350
‘Trioxygen difluoride’, 4317

HALOGENS X_2

The reactivity hazards of this well defined group of oxidants towards other materials decrease progressively from fluorine, which reacts violently with most materials (except for those metals on which resistant fluoride films form), through chlorine and bromine to iodine. Astatine may be expected to continue this trend. The individual entries are:

Bromine, 0261
Chlorine, 4041
Fluorine, 4304
Iodine, 4620

N-HALOIMIDES —CO.N(X)CO.—

Alcohols, or Amines, or Diallyl sulfide, or Hydrazine, or Xylene

Martin, R. H., *Nature*, 1951, **168**, 32

Many of the reactions of *N*-chloro- and *N*-bromo-imides are extremely violent or explosive. Those observed include *N*-chlorosuccinimide with aliphatic alcohols or benzylamine or hydrazine hydrate; *N*-bromosuccinimide with aniline, diallyl sulfide, or hydrazine hydrate; or 3-nitro-*N*-bromophthalimide with tetrahydrofurfuryl alcohol; 1,3-dichloro-5,5-dimethyl-2,4-imidazolidindione with xylene (violent explosion). Individually indexed compounds are:

N-Bromosuccinimide, 1421
Chloriminovanadium trichloride, 4159
N-Chlorosuccinimide, 1423
1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione, 1859
Potassium 1,3-dibromo-1,3,5-triazine-2,4-dione-6-oxide, 1028
Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide, 1034
1,3,5-Trichloro-1,3,5-triazinetrione, 1036

See other N-HALOGEN COMPOUNDS

2-HALOMETHYL-FURANS OR -THIOPHENES

Heterocyclic Compounds, Vol. 1, 207, Elderfield, R. C. (Ed.), New York, Wiley, 1950

The great instability of 2-bromomethyl- and 2-chloromethyl-furans, often manifest as violent or explosive decomposition on attempted distillation, is reviewed. The furan nucleus is sensitive to traces of halogen acids, and decomposition becomes autocatalytic. Individually indexed compounds are:

2,5-Bis(chloromethyl)thiophene, 2298
2-Bromomethyl-5-methylfuran, 2339
2-Bromomethylfuran, 1834
2-Chloro-5-chloromethylthiophene, 1824
2-Chloromethyl-5-methylfuran, 2345
2-Chloromethylfuran, 1835
2-Chloromethylthiophene, 1836

See also BENZYL COMPOUNDS

HALOPHOSPHINES —PHX, —PX_2

The degree of reactivity towards air or to water depends upon the degree of substitution of hydrogen by halogen. Individually indexed compound are:

* Phosphorus azide difluoride, 4309
Phosphorus trifluoride, 4333
Phosphorus triiodide, 4631
Tetrachlorodiphosphane, 4165
Tetraiododiphosphane, 4632

See related NON-METAL HALIDES, NON-METAL HYDRIDES

HALOSILANES Si_mX_n

1. Schumb, W. C. *et al., Inorg. Synth.*, 1939, **1**, 46
2. Halvorsen, F. *et al., Proc. 29th Annu. Loss Prev. Symp.*, 1995, paper 6B (Amer. Inst. Chem. Engineers)

When heated, the vapours of the higher chlorosilanes (hexachlorodisilane to dodecachloropentasilane) ignite in air. Other halo- and haloalkyl-silanes ignite without heating or have low flash points: some react violently with water [1]. An account has been given of cleaning and dismantling a plant contaminated with shock sensitive and polymeric 'oil silanes' arising as byproducts from trichlorosilane handling [2].

Individually indexed compounds are:

† Bromosilane, 0250
Decachlorotetrasilane, 4191
† Dichlorosilane, 4060
Dodecachloropentasilane, 4192
Fluorosilane, 4292
Hexachlorodisilane, 4185
Iododisilane, 4538
Octachlorotrisilane, 4188
∗ Poly(difluorosilylene), 4324
Tetrachlorosilane, 4167
† Tribromosilane, 0286
† Trichlorosilane, 4130
† Trifluorosilane, 4327

See related NON-METAL HALIDES, NON-METAL HYDRIDES

HAZARDOUS MATERIALS

1. Cloyd, D. R. *et al., Handling Hazardous Materials*, NASA Tech. Survey SP-5032, Washington, NASA, 1965
2. *Fire Protection Guide on Hazardous Materials*, SPP-1C, Boston (Ma.), NFPA, 6th edn., 1975

The survey of hazards and safety procedures involved in handling rocket fuels and oxidisers includes liquid hydrogen, pentaborane, fluorine, chlorine trifluoride, ozone, dinitrogen tetraoxide, hydrazine, methyl hydrazine and 1,1-dimethyl hydrazine [1]. The later volume [2] is a bargain compendium of five NFPA publications:

325A, *Flashpoint Index of Tradename Liquids* (8800 items), 1972

325M, *Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids* (1300 items), 1969

49, *Hazardous Chemicals Data* (416 items), 1975

491M, *Manual of Hazardous Chemical Reactions* (3550 items), 1975

704M, *Recommended System for Identification of Fire Hazards of Materials*, 1975

HAZARDS FROM PRESSURE

Hazards from Pressure: Exothermic Reactions, Unstable Substances, Pressure Relief and Accidental Discharge, Gibson, N. (ed.), IChE Symp. Ser. No. 102, Oxford, Pergamon, 1987

The 1986 UK Symposium covered hazards from pressure effects originating in various ways from exothermic runaway reactions and unstable substances, and the measures necessary to mitigate these effects. Some of the reactive hazards involved may be found under the entries:

Copper(II) acetylide(reference 2), 0612
2-Hydroxyethylamine: Carbon dioxide, etc., 0939
Sodium dithionite (reference 2), 4801
BLOWING AGENTS (reference 2)
HEAT FLOW CALORIMETRY (reference 5)
See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

HEAT FLOW CALORIMETRY

1. Hub, L., *Proc. 6th Symp. Chem. Proc. Hazards*, Symp. Ser. No. 49, 39—46, Rugby, IChE, 1977
2. Brogli, F. *et al., Runaway Reactions*, Paper 3/M, 1—10
3. Fierz, H. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, A12—A21, Rugby, IChE, 1983
4. Stockton, G. W. *et al.*, Euro-pat. Appl. EP 170713, 1986
5. Wright, T. K. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 85—96, Oxford, Pergamon, 1987
6. Burke, P. E. *Spec. Publ. – R. Soc. Chem., 195 (Pilot Plants and Scale-up of Chemical Processes)*, 1997, 52
7. Cardillo, P. *et al., Afinidad*, 1998, **55**(474), 115

As an alternative and complementary technique to the study of chemical materials by DTA, DSC, or ARC, the study of chemical processes in miniature reactors has been developed. Equipment which is sufficiently instrumented to permit full analysis of processing heat flows arising from reaction exotherms or process deviations is available, in two variants. Both have accurately controlled heating and cooling systems which are used separately or simultaneously to maintain the stirred reactor temperature at the desired level as reaction proceeds, and to indicate the heat flows from the liquid phase to the jacket and from the vapour phase to the reflux condenser etc. The first variant uses a glass flask reactor of 2 l capacity fitted with stirrer, doser and reflux condenser and can operate between —30° to +200°C under vacuum or at atmospheric pressure. Further details of the reaction safety calorimeter (RSC) and of its application to various processing problems are published [1]. The second variant has interchangeable glass vessels of 0.5 to 2.5 l operable between —20 to +200°C at up to 3 bar internal pressure, and operation and application of the bench scale calorimeter (BSC) to several different processing problems and investigations has been discussed [2,3]. Improved design features claimed include use of a zirconium reaction vessel rather than glass (10^3 increase in thermal conductivity), thermostatted feed streams and adiabatic shield [4]. The design and use of an isothermal heat flow calorimeter to assess cooling and other processing reqirements for safe operation of (semi-)batch processes are discussed. Use of this simpler type of calorimeter is complementary to that of the more expensive variable heat flow calorimeters [5].

In the 1990s, reaction calorimetry has found extensive use in industrial scale-up operations. The editor's limited exposure to it suggests that the commercially available equipment has indifferent agitation and may in consequence handle multiphase reactions poorly: anathema though they be to academic kineticists, industry finds slurries attractive. However it is a simple technique by which to acquire data on the kinetics of heat production. Publications have become very numerous, mostly publicity from testing houses offering the service. Some more recent work is found in [6,7].

See CALORIMETRY

HEAT TRANSFER

1. Bourne, J. R. *et al., Chem. Eng. Sci.*, 1987, **42**, 2183—2192
2. Bourne, J. R. *et al., Chem. Eng. Sci.*, 1987, **42**, 2193—2196

The factors which affect heat transfer from an exothermic fluid reaction system are important in determining whether a runaway reaction (thermal explosion) will ensue. Agitation reduces local heat acumulation and applied cooling affects overall heat retention and temperature of the reactor contents. Studies in unstirred vertical cylinder reactors showed the effects of convection in modifying the temperature- and flow-fields existing in a conduction-only system. An analogy between the temperature profiles in active (exothermally reacting) systems and passive (cooling without reaction) systems at equal heat-removal rates was established, offering the possibility of simpler and safer experimental assessments [1]. Correlations in a freely conducting active system show that the maximum temperature occurs just below the liquid surface, and to avoid thermal runaway, the temperature must not exceed a critical value, which depends on the heat generation rate, the liquid physical properties and the vessel size [2].

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, etc. (references 10, 11)

HEAVY METAL DERIVATIVES

This class of compounds showing explosive instability deals with heavy metals bonded to elements other than nitrogen and contains the separately treated groups:
as well as the individually indexed compounds:

Barium acetate, 1482
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3862
Cadmium propionate, 2412
* Cobalt(II) picramate, 3454
Copper(I) chloroacetylide, 1350
Diacetatotetraaquocobalt, 1774
Dicopper(I) ketenide, 0618

* Diethyllead dinitrate, 1686
Dimethylmethyleneoxosulfanenickel(0) diethylene complex, 2852
Dinitrosylnickel, 4736
* Hydroxycopper(II) glyoximate, 0795
Iron(II) maleate, 1389
Iron(III) maleate, 3441
Lanthanum 2-nitrobenzoate, 3809
Lead 2,4,6-trinitroresorcinoxide, 2064
Lead 2-amino-4,6-dinitrophenoxide, 3462
Lead bromate, 0277
Lead hyponitrite, 4740
Lead oleate, 3889
Lead(II) nitrate phosphinate, 4462
Lead(II) phosphinate, 4526
Lead(II) phosphite, 4530
Lead(II) picrate, 3430
* Lead(II) thiocyanate, 0996
Lead(II) trinitrosobenzene-1,3,5-trioxide, 3588
Manganese picrate hydroxide, 3736
Manganese(II) phosphinate, 4514
Nickel 2,4-dinitrophenoxide hydroxide, 3739
Nickel 2-nitrophenoxide, 3458
Nickel picrate, 3429
* 5-Nitrosalicylhydrazide, 2774
Scandium 3-nitrobenzoate, 3810
Silver osmate, 0034
Thallium *aci*-phenylnitromethanide, 2719
Thallium bromate, 0260
Thallium(I) 2- or 4-nitrophenoxide, 2179
Thallium(I) methanediazoate, 0457
* Thallium(I) tetraazidothallate, 4786
* Tricyclopentadienyluranium tetrahydroaluminate, 3681
Yttrium 4-nitrobenzoate trihydrate, 3811

GOLD COMPOUNDS
LEAD SALTS OF NITRO COMPOUNDS
LITHIUM PERALKYLURANATES
MERCURY COMPOUNDS
METAL ACETYLIDES
METAL FULMINATES
METAL OXALATES
PLATINUM COMPOUNDS
PRECIOUS METAL DERIVATIVES
SILVER COMPOUNDS
See also METAL AZIDES, METAL CYANIDES(AND CYANO COMPLEXES), N-METAL DERIVATIVES

HETEROCYCLIC *N*-SULFINYLAMINES Het-N=S=O

Butler, R. N. *et al., Chem. & Ind.*, 1986, 750; J. *Chem. Soc., Perk. Trans.* 2, 1989, 1855

A range of the title compounds were prepared by treating the amines with sulfinyl chloride in benzene. Purification by vacuum distillation led to violent explosions of some of those with 5 membered rings containing two or more heteroatoms on a number of occasions. It is essential to keep the distillation temperature below 60°C.

See other N—S COMPOUNDS

HEXAFLUOROCHLORONIUM SALTS $[ClF_6]^+ Z^-$

1. Christe, K. O., *Inorg. Chem.*, 1973, **12**, 1582
2. Roberts, F. Q., *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 737

These are very powerful oxidants and react explosively with organic materials or water [1]. They are not in themselves explosive, contrary to an earlier report [2].

See other OXIDANTS

HEXAMETHYLNITRATODIALUMINATE SALTS $M^+ [Al_2(Me)_6NO_3]^-$

Atwood, J. L. *et al., J. Organomet. Chem.*, 1978, **155**, 2

In the series of air-sensitive title salts, the potassium, rubidium or caesium salts ignite on exposure to air, and the tetramethyl- or tetraethyl-ammonium salts ignite with violence.

See other PYROPHORIC MATERIALS

HIGH-NITROGEN COMPOUNDS

1. *The High-Nitrogen Compounds*, Benson, F. R., New York, Wiley-Interscience, 1984
2. Bartlett, R. J., *Chem. & Ind.*, 2000, (4), 141
3. Knight, J., *New Scientist*, 2000, (2237)
4. Anon., *Chem. Brit.*, 2003, **39**(5), 19
5. Drake, G. *et al., Propellants, Explosives, Pyrotechnics*, 2003, **28**(4), 174

The major portion of the book [1] (Ch. 2, pp 2—262) deals with the thermal stability of groups of these compounds in a series of tables. The ultimate high-nitrogen compound contains only nitrogen. The fantasists of theory are hard at work imagining such molecules and advancing their claims as non-polluting propellants [2]. As yet none but old and inert dinitrogen are physical reality. Application seems improbable even should this change [3]. Study of not quite so extreme examples as explosives continues, but here too high sensitivity will usually prohibit use [4]. Some combinations of triazole bases with dinitramide as acid and oxidant may be more practical [5].

This class heading is intended to include not only those compounds containing a high total proportion of nitrogen (up to 96% by mass has been achieved) but also those containing high local concentrations in substituent groups (notably azide, diazo and diazonium) within the molecule. Many organic molecular structures containing

several chain-linked atoms of nitrogen are unstable or explosive and the tendency is exaggerated by attachment of azide or diazonium groups, or a high-nitrogen heterocyclic nucleus. Closely related but separately treated classes and groups include:
Individually indexed compounds are:

- 1-Acetyl-4-(4′-sulfophenyl)-3-tetrazene, 2977
- Aluminium azide, 0082
- Aluminium tetraazidoborate, 0059
- 5-Amino-1,2,3,4-thiatriazole, 0412
- 1-Amino-3-nitroguanidine, 0493
- 4-Amino-4*H*-1,2,4-triazole, 0808
- Aminoguanidine, 0504
- 5-Aminotetrazole, 0460
- Ammonium azide, 4521
- Azido-2-butyne, 1469
- Azidoacetonitrile, 0710
- 3,3′-Azo-(1-nitro-1,2,4-triazole), 1397
- 2,2′-Azobis(2-amidiniopropane) peroxodisulfate, 3085
- Benzotriazole, 2262
- Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-*N*3,*N*5]-(T-4) cobalt, 3862
- 3,4-Bis(1,2,3,4-thiatriazol-5-ylthio)maleimide, 2066
- Bis(1-benzo[*d*]triazolyl) carbonate, 3592
- Bis(1-benzo[*d*]triazolyl) oxalate, 3622
- 1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene, 1571
- 1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene, 0823
- 5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2827
- Carbonic dihydrazide, 0505
- Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1425
- 5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1341
- Cyanodiazoacetyl azide, 1342
- Cyanoguanidine, 0809
- Cyanohydrazonoacetyl azide, 1080
- 2,3-Diazido-1,3-butadiene, 1433
- 1,2-Diazidocarbonylhydrazine, 0716
- Diazidomethyleneazine, 1017
- Diazidomethylenecyanamide, 1013
- 2,3-Diazidopropiononitrile, 1118
- 2,6-Diazidopyrazine, 1396
- 4-Diazo-1,2,3-triazole, 0674
- 2-Diazo-2H-imidazole, 1079
- 3-Diazo-3*H*-1,2,4-triazole, 0673
- 4-Diazo-5-phenyl-1,2,3-triazole, 2905
- 3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2904
- 3-Diazo-5-phenyl-3*H*-pyrazole, 3112
- 2-Diazonio-4,5-dicyanoimidazolide, 2044
- 3-Diazoniopyrazolide-4-carboxamide, 1418
- 5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3670

1,5-Diphenylpentaazadiene, 3501
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1847
1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate, 2582
Formylhydrazine, 0472
1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1.3.5-triphosphorine, 4789
Hydrazinium azide, 4545
Hydrazinium chloride, 4001
5-Hydrazino-1,2,3,4-thiatriazole, 0461
5,5′-Hydrazotetrazole, 0822
1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0813
1-Hydroxybenzotriazole, 2265
* Lithium hexaazidocuprate(4—), 4272
* Lithium tetraazidoaluminate, 0081
* Lithium tetraazidoborate, 0151
Methyl 3,3-diazido-2-cyanoacrylate, 1818
1-Methyl-1,2,3-triazole, 1185
Methylenebis(3-nitramino-4-methylfurazan), 2801
3-Nitro-1,2,4-triazolone, 0712
Nitrosyl azide, 4761
Pentazole, 4437
N-Phenyl-1,2,3,4-thiatriazolamine, 2725
3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2800
Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2249
Sodium 5-azidotetrazolide, 0548
* Sodium hexaazidophosphate, 4788
Tetraallyl-2-tetrazene, 3539
* *trans*-Tetraamminediazidocobalt(III)*trans*-diamminetetraazidocobaltate(1—), 4214
Tetraazido-1,4-benzoquinone, 2629
Tetraimide, 4522
1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene, 3008
Tetramethyl-2-tetrazene, 1753
1,3,6,8-Tetraphenyloctaazatriene, 3843
1,2,4,5-Tetrazine, 0711
2,4,6-Triazido-1,3,5-triazine, 1344
1,2,4-Triazole-3-diazonium nitrate, 0676
1,3,5-Triphenyl-1,4-pentaazadiene, 3748

See also Pentazonium hexafluorarsenate
AZIDES (in several groups)
DIAZO COMPOUNDS
DIAZOAZOLES
DIAZONIUM SALTS (in several groups)
N—NITRO COMPOUNDS
PENTAZOLES
TETRAZENES
TETRAZOLES

TRIAZENES
TRIAZOLES

HIGH PRESSURE REACTION TECHNIQUES

1. Rooymans, C. J. M. in *Preparative Methods in Solid State Chemistry*, Hagenmuller, P. (Ed.), New York, Academic Press, 1972
2. *High Pressure Safety Code*, London, High Pressure Association, 1975
3. Paauwe, J., *High Press. Technol.*, 1977, **1**, 13—28
4. Jercinovic, L. M., *Plant/Oper. Progr.*, 1984, **3**, 34—37
5. Mehne, P. H., *Plant/Oper. Progr.*, 1984, **3**, 37—39
6. Franko-Filipasic, B. R. *et al., Chem. Eng. Progr.*, 1984, **8**0(3), 65—69
7. Livingston, E. H., *Chem. Eng. Progr.*, 1984, **80**(3), 70—75
8. Sherman, W. F., *Experimental Techniques in High-pressure Research*, New York, Wiley, 1987

The chapter which reviews high-pressure (HP) techniques in liquid and gas systems for preparative purposes also includes safety considerations [1]. The Code deals mainly with mechanical hazards, but attention is drawn to the fact that application of HP to chemical systems may influence stability adversely [2]. The forces and energy involved in HP systems, and the causes and elimination of accidents in HP operations are reviewed [3]. Design procedures and checklists [4] and training methods [5] relevant to safety in HP operations are discussed. The design features of two HP resesarch laboratories are detailed, including use of remote manipulation for hazardous reaction studies [6]. Operational factors to minimise hazards in HP facilities, including operator training, equipment inspection and maintenance, are presented [7]. A new handbook deals with the design, construction and safe operation of equipment for research at high pressures [8].

HIGH RATE DECOMPOSITION

Gibson, N. *et al., Runaway Reactions*, 1981, Paper 3/R, 1—14

Some compounds not classified as deflagrating or detonating explosives can decompose violently (deflagrate), and account of this must be taken in designing powder handling plant, which is now usually totally confined. Compounds of this type, often with an oxygen balance around —200, usually decompose when heated with a high rate of decomposition. Those compounds below were examined for ease of initiation when exposed to friction or localised heating, in both open or closed systems. Individually indexed compounds are:

2-Acetylamino-3,5-dinitrothiophene, 2273
2-Amino-3,5-dinitrothiophene, 1417
4-Bromo-2,6-dinitroaniline, 2126
2-Bromo-4,6-dinitroaniline, 2125
2-Chloro-4,6-dinitroaniline, 2146
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1948
2-Formylamino-3,5-dinitrothiophene, 1817
2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate, 3234
2-Methoxyanilinium nitrate, 2825

1,5-(or 1,8-)Bis(dinitrophenoxy)-4,8-(or 4,5-)dinitroanthraquinone, 3854
See entry CRITICAL IGNITION TEMPERATURE, DEFLAGRATION INCIDENTS

HIGH SURFACE-AREA SOLIDS

Smith, E. A., *Processing*, 1977, (11), 35—37

The reactivity of solids may change dramatically as they are ground to sub-micron sizes. Graphite becomes pyrophoric at 400 m^3/g, and if ground under nitrogen to 600 m^3/g, cyanogen is produced by direct combination of the elements. Sulfur becomes highly reactive at lower micron sizes, and iron becomes liable to explosive oxidation when ground to below 1 μ. Theoretical aspects of the great increase in surface energy are discussed.

HIGH VALENCY METAL FLUORIDES

Dukat, W. W., *et al., J. Chem. Soc., Chem. Comm.*, 1993, (18), 1429

High valency transition metal fluorides may react violently with organic materials, not only by fluorinating, C-H bonds but also by exchange reactions with organochlorine compounds. Thus osmium and iridium hexafluorides reacted explosively with a fewfold excess of dichloromethane, unless judiciously cooled with liquid nitrogen, even at sub-gram scale. Such compounds usually also react vigorously with water and other nucleophiles (Editor’s comment).

HOPCALITE

Kirk-Othmer, 1996, Vol. 17, 216

An oxidation catalyst containing cobalt, copper, manganese and silver species. It adsorbs nitroalkanes strongly, which may then ignite. Respirator cartridges containing it should not be used in high concentrations of nitroalkanes.
See NITROALKANES

HYDRAZINE METAL MALONATES AND SUCCINATES

1. Sivasankar, B. N. *et al., Synth. React. Inorg. Met.-Org. Chem.*, 1994, **24**(9), 1573
2. Sivasankar, B. N. *et al., Mater. Res. Bull.*, 1996, **31**(1), 47

Several octahedral dihydrazine metal (II) salts of this class were prepared and thermally decomposed. The succinates and malonates of nickel and cadmium decomposed explosively [1]. A later paper on mixed metal bis-hydrazine malonates of cobalt with magnesium, manganese, nickel, zinc or cadmium recommends that decomposition, in a pre-heated crucible at 500°C, be of small quantities only. The same workers have reported exothermic decomposition of similar hydrazine complexed salts of other small organic acids.

HYDRAZINEMETAL NITRATES $[(H_4N_2)_mM][NO_3]_n$

1. Médard, L. *et al., Mém. Poudres*, 1952, **34**, 159—166
2. Patel, K. C. *et al, Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**(4), 383

Hydrazine complexes of cadmium, cobalt, manganese, nickel and zinc nitrates were prepared as possible initiator materials. Dihydrazinemanganese(II) nitrate ignites at 150°C but is not shock-sensitive, while trihydrazinecobalt(II) nitrate, which decomposes violently at 206—211°C or in contact with conc. acids, and trihydrazinenickel(II) nitrate (deflagrates at 212—215°C) are fairly shock-sensitive. Trihydrazinecadmium nitrate (defl. 212—245°C) and trihydrazinezinc nitrate are of moderate and low sensitivity, respectively [1]. A later study covers the same ground, adding trihydrazineiron(II) nitrate and dihydrazinecadmium(II) nitrates to the list of potential primary explosives, but reporting the dihydrazinemagnesium salt as not shock-sensitive. This work also covered some dihydrazinemetal azides and perchlorates, those of Mg were not shock sensitive but the azides of Co, Ni, and Zn were [2]. The combination of an endothermic fuel, an oxidant and catalytic metals — mostly having 1 electron transitions capable of initiating radical reactions — might be predicted to be sensitive.

See Trihydrazinenickel(II) nitrate

See other AMMINEMETAL OXOSALTS

HYDRAZINIUM AZIDES

Hammerl, A. *et al., Z. Anorg. Allg. Chem.* 2001, **62**(7), 1477

A variety of organic hydrazine azides were studied. Only the stronger bases gave isolable solid azides. Most were surprisingly stable, insensitive to shock and friction, but giving vigorous decomposition on heating – if the salt did not first dissociate. There was a tendency to lose ammonia on standing.

HYDRAZINIUM SALTS $H_2NN^+H_3\ Z^-$

1. Mellor, 1940, Vol. 8, Suppl. 2.2, 84—86
2. Salvadori, R., *Gazz. Chim. Ital. [2]*, 1907, **37**, 32
3. Levi, G. R., *Gazz. Chim. Ital. [2]*, 1923, **53**, 105

Several salts are explosively unstable, including hydrazinium azide (explodes on rapid heating or on initiation by a detonator, even when damp), chlorate (explodes at m.p., 80°C), chlorite (also highly flammable when dry), hydrogen selenate, hydrogen sulfate (explodes when melted), nitrate, nitrite, and the highly explosive perchlorate and diperchlorate used as propellants [1,2,3].

Hydrazine salts with nitrous acid, metal nitrites or nitrite esters readily form hydrazoic acid.

Some examples are:

1,1-Diphenylhydrazinium chloride, 3513
Hydrazinium azide, 4545
Hydrazinium chlorate, 4004
Hydrazinium chloride, 4001
Hydrazinium chlorite, 4002
Hydrazinium dinitrate, 4556
Hydrazinium diperchlorate, 4062
Hydrazinium hydrogen selenate, 4553
Hydrazinium nitrate, 4544

Hydrazinium nitrite, 4543
Hydrazinium perchlorate, 4005

See also Hydrogen azide

See PROPELLANTS, REDOX COMPOUNDS

HYDRAZONES $RR'C{=}NNH_2$

Glycols, Alkali hydroxides

1. Todd, D., *Org. React.*, 1948, **IV**, 8

This mixture is the Huang Minlon modification of the Wolff Kishner reaction. In the editor's experience it often leaps from the flask with sudden gas evolution. In addition to the expected nitrogen, at the operating temperature of around 200°C it is uncomfortably near the temperature of hydrogen evolution from glycol decomposition. The reduction proceeds much cooler in dimethyl sulfoxide or some of the alkoxyethanols as solvent.

See Sodium hydroxide: Glycols

HYDROGENATION CATALYSTS

1. Augustine, R. L., *Catalytic Hydrogenation*, 23, 28, London, Arnold, 1965
2. Anon., *Chem. Brit.*, 1974, **10**, 367
3. Poles, T., private comm., 1973
4. Freifelder, 1971, 74, 78, 81—83, 168, 175, 262, 263
5. Jimenez, M. H., *Org. Prep. Proced. Int.*, 1978, **10**, 295—297

Many hydrogenation catalysts are sufficiently active to effect rapid interaction of hydrogen and/or solvent vapour with air, causing ignition or explosion. This is particularly so where hydrogen is adsorbed on the catalyst, either before a hydrogenation (Raney cobalt, nickel, etc.), or after a hydrogenation during separation of catalyst from the reaction mixture. Exposure to air of such a catalyst should be avoided until complete purging of hydrogen with an inert gas, such as nitrogen, has been effected. With catalysts of high activity and readily reducible substrates, control of the exotherm may be required to prevent runaway reactions, particularly at high pressures [1]. A proprietary form of Raney nickel catalyst in which the finely divided metal particles are coated with a fatty amine is claimed to be free of pyrophoric hazards if it dries out [2].

Platinum-metal catalysts are preferably introduced to the reactor or hydrogenation system in the form of a water-wet paste or slurry. The latter is charged to the empty reactor: air is removed by purging with nitrogen or by several evacuations alternating with nitrogen filling: the reaction mixture is charged, after which hydrogen is admitted. The same procedure applies where it is mandatory to charge the catalyst in the dry state, but in this case the *complete* removal of air before introduction of the reaction mixture and/or hydrogen is of vital importance.

Platinum, palladium and rhodium catalysts are non-pyrophoric as normally manufactured. Iridium and, more particularly, ruthenium catalysts may exhibit pyrophoricity in their fully reduced form, and for this reason are usually manufactured in the unreduced form and reduced in situ. Spent catalysts should be purged from hydrogen and washed free from organics with water before storage in the water-wet condition. Under no circumstances should any attempt be made to dry a spent catalyst [3].

Specialist advice on safety and other problems in the use of catalysts and associated equipment is freely available from Engelhard Industries Ltd. at Cinderford in Gloucester, where a model high-pressure hydrogenation laboratory with full safety facilities is maintained.

In a volume devoted to hydrogenation techniques and applications, there are several references to safety aspects of catalytic hydrogenation. For noble metal and nickel catalysts, low boiling solvents should be avoided to reduce the risk of ignition when catalysts are added. Risks are highest with carbon-supported catalysts, which tend to float at the air interface of the solvent. The need for dilute solutions of nitro- and polynitro-aromatics or oximes, and for relatively low concentrations of catalysts to minimise the relatively large exotherms, are stressed [4]. A simple syringe-filter apparatus is described, which permits hazard-free rinsing, near-drying and transfer of palladium black catalysts [5].

Individually indexed catalysts are:

Iridium, 4638
Lanthanum—nickel alloy, 4673
Nickel, 4814
Palladium, 4879
Platinum, 4881
Rhodium, 3528
Ruthenium, 4888

See CATALYTIC NITRO REDUCTION PROCESSES, COPPER CHROMITE CATALYST, HYDROGEN TRANSFER

See also HYDROGENATION INCIDENTS

HYDROGENATION INCIDENTS

Harak, J., *Stud. Sur. Sci. Catal.*, 1986, **27** (Catal. Hydrog.), 579—511

A comprehensive discussion of parameters and methods necessary for effective control of laboratory and industrial scale hydrogenation autoclaves, and the need for early recognition of hazardous situations is available.

For hazardous incidents involving hydrogenation,
and the individual entries:

† Benzene, : Hydrogen, Raney nickel, 2281
Formic acid, : Palladium—carbon catalyst, 0417
† Hydrogen (Gas), : Acetylene, Ethylene, 4447
† Hydrogen (Gas), : Catalysts, Vegetable oils, 4447
† Hydrogen (Gas), : Ethylene, Nickel catalyst, 4447
† Hydrogen (Gas), : Palladium, 2-Propanol, 4447
Hydrogen peroxide, : Hydrogen, Palladium catalyst, 4471
3-Methyl-2-penten-4-yn-1-ol, 2378
1,1,1-Tris(azidomethyl)ethane, 1931
Tris(hydroxymethyl)nitromethane, 1658

See CATALYTIC NITRO REDUCTION PROCESSES, HYDROGEN TRANSFER

See also CATALYTIC HYDROGENATION AUTOCLAVES
See other UNIT OPERATION OR UNIT PROCESS INCIDENTS

HYDROGEN TRANSFER

1. Editor's comments, 2005
2. West, A. V. *et al., Org. Proc. Res. & Dev.*, 2002, **6**(3), 304

A hydrogen transfer reaction is, effectively a catalytic hydrogenation in which the hydrogen is generated in situ from some material capable of undergoing a retro-hydrogenation with the hydrogenation catalyst. Academic literature often commends such methods as safer than handling hydrogen. Industry finds the latter a slight problem and notes that transfer methods are seldom as effective and, unless internal, generate waste. Although less energetic than corresponding hydrogenations, thermodynamics requires that any useful reaction has significant free energy. Hydrogenations can be controlled by stopping either the hydrogen supply, or the agitation which mixes gas and liquid phases. Transfer methods operated, as usual, with everything in the pot from the start lack either control. There can be the potential to pressurise a reactor from overheating a solvent or volatile reagent. It is usual that catalyst appears more active when an hydrogenation reaction is scaled up (less inhibitor on proportionately smaller reactor surfaces) [1]. A unexpectedly rapid temperature rise was observed when converting an unsaturated alcohol to the saturated ketone. It is recommended that internal transfer reactions be considered whenever hydrogenation catalysts are employed in reactions to be scaled up [2].

HYDROXOOXODIPEROXOCHROMATE SALTS $M[HOCr(O_2)_2O]$

Bailar, 1973, Vol. 3, 699

The ammonium, potassium, and thallium salts are all violently explosive. The entries are:

Ammonium hydroxooxodiperoxochromate(1—), 4224
Potassium hydroxooxodiperoxochromate(1—), 4221
Thallium hydroxooxodiperoxochromate(1—), 4222
See other PEROXOACID SALTS

HYDROXYLAMINIUM SALTS $HON^+H_3\ Z^-$

Anon., *Chem. Processing (Chicago)*, 1963, **26**(24), 30

Some decompositions of salts of hydroxylamine are discussed, including violent decomposition of crude chloride solutions at 140° and exothermic decomposition of the solid sulfate at 170°C. The phosphinate and nitrate decompose violently above 92 and 100°C, respectively.

Some examples are:

Hydroxylaminium chloride, 3996
Hydroxylaminium nitrate, 4519
Hydroxylaminium perchlorate, 3999
Hydroxylaminium phosphinate, 4550
Hydroxylaminium sulfate, 4570

∗ *N*-(Methylphenylphosphinoyl)hydroxylamine, 2819
See Sodium nitrite
See other N—O COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

3-HYDROXYTRIAZENES N=N—NOH

Houben-Weyl, 1965, Vol. 10.3, 717

Many of the 3-hydroxytriazene derivatives produced by diazo-coupling onto *N*-alkyl or *N*-aryl hydroxylamines decompose explosively above their m.p.s. However, the heavy metal derivatives are stable and used in analytical chemistry.

See other TRIAZENES

HYPOHALITES ROX

1. Sidgwick, 1950, 1218
2. Chattaway, F. D., *J. Chem. Soc.*, 1923, **12**3, 2999
3. Anbar, M. *et al., Chem. Rev.*, 1954, **54**, 927
4. Lewis, D. J., private comm., 1983
5. Suzuta, T., *Chimica Oggi,* 2003, **21**(5), 62

This class of organic oxidant compounds, all containing O—X bonds, includes widely differing types and many compounds of limited stability. Alkyl hypochlorites, readily formed from alcohols and chlorinating agents, will explode on ignition, irradiation or contact with copper powder [1,2]. Of the many alkyl hypohalites described, only ethyl, *tert*-butyl and *tert*-pentyl are stable enough to isolate, purify and handle [3], though care is needed. Some of the lower alkyl hypochlorites are not as unstable or hazardous as was formerly thought [4]. Simple alkyl hypofluorites are unpredictably explosive, some samples explode on warming to —80°C; methyl, ethyl, deuteroethyl and *tert*-butyl are recorded [5]. There are the separately treated groups:
and the individually indexed compounds:

∗ Bromine(I) trifluoromethanesulfonate, 0311
∗ Chlorine fluorosulfate, 3969
∗ Chlorine(I) trifluoromethanesulfonate, 4041
∗ Chloroperoxytrifluoromethane, 0318
Chloryl hypofluorite, 3967
Difluoromethylene dihypofluorite, 0354
Ethyl hypochlorite, 0847
Fluorine perchlorate, 3970
Heptafluoroisopropyl hypofluorite, 1031
Heptafluoropropyl hypofluorite, 1057
Hypochlorous acid, 3989
Isopropyl hypochlorite, 1243
Methyl hypochlorite, 0433
Methyl hypofluorite, 0441
Nitryl hypochlorite, 4020
Pentafluoroselenium hypofluorite, 4362
Pentafluorosulfur hypofluorite, 4361
∗ Pentafluorosulfur peroxyhypochlorite, 3984

Pentafluorotellurium hypofluorite, 4363
* Perfluoro-*tert*-butyl peroxyhypofluorite, 1369
Tetrafluoroiodosyl hypofluorite, 4350
Trifluoromethyl hypofluorite, 0352

See also ACYL HYPOHALITES, BIS(FLUOROOXY)PERHALOALKANES

IGNITION SOURCES

1. Howard, W. B., *Chem. Eng. Progr.*, 1970, **66**(9), 59—65
2. Enstad, G., *Reconsideration of the Concept of Minimum Ignition Energy*, Euro. Fed. Chem. Engrs. Wkg. Party, March 16th 1975
3. Kashiwagi, T., *Combustion Sci. Technol.*, 1980, **21**(3—4), 131—139
4. *Guidance on RF Ignition Hazards*, GS21, HMSO, 1983
5. Anon., *Fire Prev.*, 1983, **165**, 27—31
6. Baev, V. K. *et al., Chem. Abs.*, 1984, **100**, 54018
7. McMillan, A. J., *Meas. Control*, 1986, **19**(7), 41—45
8. Anon., *Fire Prev.*, 1986, (194), 45
9. Bernard, F., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 683—704, Heidelberg, ISSA, 1987
10. *Ignition of Solids*, Vlyanov, V. L., Zarko, V. E., Amsterdam, Elsevier, 1989
11. *Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991
12. Carson, P. A. *et al., Loss Prev. Bull.*, 1992, 108
13. Carleton, F. B. *et al., Proc. Roy. Soc. London, Ser. A.*, 1994, **447**(1931), 513
14. *Learning from Accidents in Industry*, Keltz, T.A. , London, Butterworths, 1998, p. 32

Some plant incidents involving unexplained ignition sources are detailed [1]. The reason why less energetic sparks will ignite a dust cloud while more energetic sparks will not is that the latter expel dust particles from the ignition zone, while the former do not [2]. The ignition of liquid decane under high intensity CO_2 laser irradiation (1—5 kW/cm^2) was studied [3], as was ignition of flammable atmospheres by laser beams emergent from optical fibres for various wavelengths and targets [13]. A guide outlining the risks of RF radiation as ignition sources was published [4]. In a discussion of the principles affecting spark ignition of flammable gases and vapours, minimum ignition energies for 60 such materials are included [5]. Under certain conditions involving shock waves, hydrogen or methane released from cylinders at 20—200 bar into an air-filled chamber at 15°C/1 bar may ignite spontaneously [6].

BS 6656:1986, dealing with hazards of ignition by sparks induced by electromagnetic transmissions (radio, television, radar), is discussed in relation to the chemical, petrochemical and oil industries. For hydrogen, any transmission above 2 W radiated power is a potential ignition source [7]. An explosion in a spray drier producing powdered milk was initiated by mechanical failure of the atomiser head, rotating at 7,500 rpm and causing frictional sparks [8]. Causes of 2 cases of ignition at LPG filling stations were analysed. In one, ignition of propane occurred when filling clamps were applied to the cylinder, and in the second, ignition of butane occurred when a connecting hose burst [9]. Various aspects of the ignition of solids are covered in a book [10]. For an excellent summary of known causes of ignition in industry, with numerous case histories and some tables of properties [11].

A study of mechanisms and circumstances of spontaneous combustion with incidents and a list of susceptible materials [12]. Water is often involved.

As with other self-propagating nucleated processes, the probability of fire increases with the volume of the system. On large industrial scale it should be asumed that a source of ignition will be present so effort must be given to minimising combustible volumes [14]. Unexpected sources of ignition have led to many fires and explosions, usually in cases of leakage or spillage of flammable materials. Some examples are:
Aluminium—magnesium alloy: Iron(III) oxide, Water, 0053
Aluminium—magnesium—zinc alloy, : Rusted steel, 0054
Carbon dioxide, : Flammable materials, 0554
Carbon dioxide, : Metals, 0554
† Ethylene, : Steel-braced tyres, 0777
Oxygen (Liquid), : Asphalt, 4826
† Sulfur, : Static discharges, 4891
FRICTIONAL IGNITION OF GASES AND VAPOURS
FRICTIONAL INITIATION OF DUST CLOUDS
GRAVEL
IRRADIATION DECOMPOSITION INCIDENTS
SELF HEATING AND IGNITION INCIDENTS

INCINERATOR DUST

See Diprotium monoxide: Incinerator dust

INDIGESTION

1. Kimura, I. *et al., Chem. Abs.*, 1993, **119**, 85759c
2. Sidebotham, G., *Chem. Phys. Processes Combust.*, 1995, 463

The afflatus of the human gut consists of carbon dioxide and hydrogen (not methane). A Japanese study of hydrogen generation as a hazard of bowel lavage solutions and a laxative is abstracted. Most produced hydrogen, especially the laxative, when incubated with dog faeces [1]. Use of nitrous oxide as an anaesthetic generates flammable gas mixtures in the intestines. Surgery with potential sources of ignition is to be avoided [2].
Hydrogen(Gas), 4447
See Dinitrogen oxide
See also BATS

INDUCTION PERIOD INCIDENTS

In the absence of anything to prevent it, a chemical reaction will begin when the components and any necessary energy of activation are present in the reaction system. If an inhibitor (negative catalyst or chain-breaker) is present in the system, it will prevent the onset of normal reaction until the concentration of the inhibitor has been reduced by decomposition or side reactions to a sufficiently low level for reaction to begin. This delay in onset of reaction is termed the induction period.

The existence of an induction period can interfere significantly with the course of a reaction where this involves either control of the rate of reaction by regulating the rate of addition of one of the reagents, or of the reaction temperature. In the absence of reaction, the concentration of the added reagent (or the temperature) may be increased to a level at which, once reaction does begin, it may accelerate out of control and become hazardous. It is essential, therefore, in the early stages of a reaction to ensure that the desired transformation has begun, particularly if large quantities of material are involved. This may be achieved by watching for a change in colour or appearance in the reaction mixture, for an increase in the rate of heat evolution (as judged from reflux rate, need for cooling, etc.), or by removal of a sample for chemical or instrumental testing.

Grignard reagents are notorious for the existence of induction periods, and an extensive account of methods for their elimination by various activation procedures is given at the beginning of the treatise on Grignard reactions by Kharasch and Reinmuth (1954). Another long-used method of promoting the onset of reaction in on-going processes is the addition to the reaction mixture of a small quantity of reaction mixture kept from a previous batch. When organolithium reagents were made from the metal and alkyl halides, they had an even worse reputation than Grignard reagents

Some relevant examples may be found in the group entries:
and in the individual entries:

† Acrylaldehyde, 1142
Aluminium tetrahydroborate, : Alkenes, Oxygen, 0058
Benzeneseleninic acid, : Hydrazine derivatives, 2328
Benzyltriethylammonium permanganate, 3611
Bis(4-hydroxyphenyl) sulfone, 3491
tert-Butyllithium, : 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine, 1647
Calcium acetylide, : Methanol, 0582
* 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2970
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2664
2,6-Dibromobenzoquinone-4-chloroimide, 2069
Dichlorine oxide, 4089
2,6-Dichlorobenzoquinone-4-chloroimide, 2071
Diethyl acetylenedicarboxylate, 2982
Dimethyl 2-chloro-4-nitrophenyl thionophosphate, 2955
Dimethyl 3-chloro-4-nitrophenyl thionophosphate, 2956
Dimethyl 4-nitrophenyl thionophosphate, 2974
† Dimethyl sulfoxide, 0917
N,N-Dimethyl-4-nitrosoaniline, : Acetic anhydride, Acetic acid, 2975
4,6-Dinitro-1,3-benzenediol, 2191
2,4-Dinitrotoluene, 2722
Fluorine, : Water, 4304
Hydrogen chloride, : Chlorine, Dinitroanilines, 3987
Hydrogen peroxide, 4471
Hydrogen peroxide, : Nitrogenous bases, 4471

Lead(IV) oxide, : Carbon black, Chlorinated paraffin, 4828
Magnesium, : Methanol, 4685
Manganese(IV) oxide, 4700
Mercury(I) azide, 4607
† Methanol, : Carbon tetrachloride, Metals, 0482
† Methyl acrylate, 1526
Nitric acid, : 1,3-Diacetoxybenzene, 4430
Nitric acid, : Formic acid, 4430
Phosphorus trichloride, 4147
Potassium dioxide, 4651
Potassium ethoxide, 0857
Sodium chlorite, : Phosphorus, 4032
Sodium dichromate, : Acetic anhydride, 4244
Sodium tetrahydroborate, : Dimethyl formamide, 0147
Succinodinitrile, 1429
† Tetracarbonylnickel, : Oxygen, Butane, 1799
2,4,6-Trichloro-1,3,5-triazine, : Dimethylformamide, 1035
2,4,6-Tris(bromoamino)-1,3,5-triazine, 1088
Zinc, : Water, 4921

ALKYL NITRATES: Lewis acids
DIALKYLZINCS
GRIGNARD REAGENTS
OXIME CARBAMATES

INHERENT SAFETY

1. Kletz, T. A. *Chem. Engineering*, 1976, **83**(8), 124
2. Gentile, M. *et al., Process Safety & Environ. Protection*, 2003, **81**(B6), 444
3. Shah, S. *et al., Process Safety & Environ. Protection*, 2003, **81**(B6), 430
4. Sanders, R. E., *J. Haz. Mat*, 2003, **104**(1-3), 149
5. Kletz, T. A. *Cheaper, Safer Plants*, Rugby, IChE, 2nd Edn. 1985

When designing a chemical process and equipment to operate it, the usual industrial approach has been to assure that nothing will go wrong by addition of numerous safety features. In operation, sooner or later something will go wrong and those added safety features may then be found either not to work, or to have been turned off. An alternative mindset is to be sure that, at sometime, everything will go wrong and to ensure that, even so, the consequences can not be serious. This is inherent safety. It is not a 21st century concept [1,5], but the new century finds the term ever more in use [4]. A principal element is always inventory reduction, so academic chemists trend towards inherent safety whenever they recommend that dangerous materials should be handled only in milligram quantities. Paradoxically, chemistry graduates trained only on that scale will be inherently unsafe should they later enter manufacturing industry. In chemical engineering terms, also, the detail can be confused, an attempt to apply fuzzy logic to index inherent safety is reported [2]. Other classifications are also attempted [3].

See also SCALE OF WORK

INORGANIC ACIDS H^+

Many of the inorganic (mineral) acids have been involved in various incidents, either as catalysts or reactants, the most common, so far as frequency is concerned, being nitric acid in oxidation incidents. Individual acids are:

Amidosulfuric acid, 4494
* Bismuthic acid, 0228
Boric acid, 0144
Bromic acid, 0248
Chlorosulfuric acid, 3991
Chromic acid, 4223
Diamidophosphorous acid, 4542
Dioxonium hexamanganato(VII)manganate, 4548
Fluorophosphoric acid, 4291
Fluoroselenic acid, 4289
Hydriodic acid, 4417
Hydrogen azide, 4435
Hydrogen bromide, 0247
Hydrogen chloride, 3987
Hydrogen fluoride, 4288
Hydrogen hexafluorophophosphate, 4354
Iodic acid, 4418
Nitric acid, 4430
Nitrosylsulfuric acid, 4432
Nitrous acid, 4429
Orthoperiodic acid, 4537
Orthophosphoric acid, 4500
Pentafluoroorthoselenic acid, 4348
Perchloric acid, 3992
Periodic acid, 4419
Permanganic acid, 4428
Peroxomonophosphoric acid, 4501
Peroxomonosulfuric acid, 4475
Phosphinic acid, 4498
Phosphonic acid, 4499
* Sodium hydrogen sulfate, 4440
Sulfuric acid, 4473
Tetrafluoroboric acid, 0130
Tetraphosphoric acid, 4562
See ORGANIC ACIDS

INORGANIC AZIDES EN_3, MN_3

1. Mellor, 1967, Vol. 8, Suppl. 2, 42
2. Evans, B. L. *et al., Chem. Rev.*, 1959, **59**, 515
3. Deb, S. K. *et al., Proc. 8th Combust. Symp.*, 1960, 289

Relationships existing between structure, stability and thermal, photochemical and explosive decomposition (sometimes spontaneous) of the inorganic azides has been extensively investigated and reviewed [1,2]. The ignition characterisitcs of explosive inorganic azides, with or without added impurities under initiation by heat or light have been discussed [3].

Relevant groups of inorganic azides are:

HALOGEN AZIDES
METAL AZIDE HALIDES
METAL AZIDES
NON-METAL AZIDES

INORGANIC BASES OH^-

Several of the inorganic bases have been involved in various laboratory or industrial scale incidents, individual entries being:

† Ammonia, 4492
Ammonium hydroxide, 4539
Barium hydroxide, 0208
Caesium amide, 4254
Calcium carbonate, 0316
Calcium hydroxide, 3922
Calcium oxide, 3931
Lead carbonate—lead hydroxide, 0722
Lithium carbonate, 0530
Magnesium carbonate hydroxide, 0531
Magnesium oxide, 4690
Potassium carbonate, 0528
Potassium hydroxide, 4422
Sodium carbonate, 0549
Sodium hydroxide, 4439
Sodium oxide, 4796

INORGANIC PEROXIDES O_2^{2-}

1. Castrantas, 1970
2. Castrantas, 1965

The guide to safe handling and storage of peroxides also contains a comprehensive bibliography of detailed information [1]. The earlier publication contains tabulated data on fire and explosion hazards of inorganic peroxides [2].

Hydrogen peroxide, 4471
PEROXOACID SALTS
PEROXOACIDS
See METAL PEROXIDES

INSULATION

1. Britton, L. G., *Plant/Oper. Progr.*, 1991, **10**(3) 27
2. McDermott, P. E., *Chem. Brit.*, 1976, **12**, 69

3. Markham, H., *Chem. Brit.*, 1976, **12**, 205
4. Carrettes, G. V., *Chem. Brit.*, 1976, **12**, 204
5. Hilado, C. J., *J. Fire Flamm.*, 1974, **5**, 326—333
6. Bowes, P. C., *Fires in Oil-Soaked Lagging*, CP35/74, Garston, Building. Res. Establ., 1974
7. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 32
8. McIntosh, A. C. *et al., J. Chem. Soc., Faraday Trans.*, 1996, **92**(16), 2965
9. Brindley, J. *et al., Process Saf. Environmental Prot.*, 1999, **77**(B2), 61

The porous and absorbent materials commonly used to lag industrial reactors may present active surfaces for the reaction of leaked contents with themselves or air. Resultant hotspots or fires can have devastating consequences, especially when endothermic materials are within. A study of exotherm and autoignition (from start temperatures as low as 65°C) of several polyamines, glycols, olamines and other compounds is detailed, together with an empirical method for predicting hazards from flash points and autoignition temperatures [1]. In these circumstances the temperature of ignition is often well below the conventionally determined AIT. Experiments showed an ignition temperature some 100—200°C below the AIT, depending on the nature of the oils and of the lagging material into which they were soaked [2]. The experimental technique was criticised on the grounds that excess air is supplied to the sample, whereas in practice access of air is often severely limited. An alternative procedure to simulate practice more closely is described, and the results for leakage of heat-transfer oils are given, ignition generally occurring at 160—200°C. The need for care to avoid fire when removing oil-contaminated lagging is stressed [3].

Attention was drawn to the existing test for the self-heating properties of textile oils, and the promoting (co-oxidant) effect of iron or copper in reducing the AIT of the oils [4]. The presence of combustibles incorporated into lagging materials during manufacture can give rise to significant self-heating effects in uncontaminated lagging [5]. The theoretical background and current experimental progress were reviewed [6]. Two incidents involving ignition of PCB heat transfer oil on calcium silicate lagging were reported. Foamed glass lagging appears to be advantageous for high-risk areas [7]. A computer model of lagging fire ignition has been developed and tested against hydrocarbon liquids [8,9].

See Ethylene oxide

See also PACKAGING INCIDENTS

INTERHALOGENS

Kirk-Othmer, 1966, Vol. 9, 585—598

The fluorine-containing members of this group are oxidants almost as powerful as fluorine itself. Individually indexed compounds are:

Bromine fluoride, 0238
Bromine pentafluoride, 0243
Bromine trifluoride, 0241
Chlorine fluoride, 3965
Chlorine pentafluoride, 3983
Chlorine trifluoride, 3975

Iodine bromide, 0254
Iodine chloride, 4007
Iodine heptafluoride, 4372
Iodine pentafluoride, 4349
Iodine trichloride, 4133

IODINE COMPOUNDS

Several iodine compounds are explosively unstable, individually indexed compounds being:

3-Acetoxy-4-iodo-3,7,7-trimethylbicyclo[4.1.0]heptane, 3538
Ammonium iodate, 4508
Ammonium periodate, 4509
Azidoiodoiodonium hexafluoroantimonate, 4355
[*I,I*-Bis(trifluoroacetoxy)iodo]benzene, 3233
Boron triiodide, 0150
4-*tert*-Butyliodylbenzene, 3313
Caesium tetraperchloratoiodate, 4155
Calcium 2-iodylbenzoate, 3618
Dicyanoiodonium triflate, 1045
Diiodamine, 4420
1,2-Diiodobenzene, 2165
3,5-Dimethyl-4-[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole, 3109
* 2-Ethoxy-1-iodo-3-butene, 2443
Hexamethylenetetramine tetraiodide, 2465
(Hydroxy)(oxo)(phenyl)-λ^3-iodanium perchlorate, 2292
Iodic acid, 4418
Iodinated poly(sulfur nitride), 4617
Iodine azide, 4616
Iodine bromide, 0254
Iodine chloride, 4007
Iodine dioxide trifluoride, 4328
Iodine heptafluoride, 4372
* Iodine isocyanate, 0521
Iodine pentafluoride, 4349
Iodine triacetate, 2388
Iodine(III) perchlorate, 4134
Iodine(V) oxide, 4622
Iodine(VII) oxide, 4623
4-Iodo-3,5-dimethylisoxazole, 1862
3-Iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0]heptane, 3406
Iodobenzene, 2242
Iododisilane, 4538
2(2-Iodoethyl)-1,3-dioxolane, 1922
1-Iodohexa-2,4-diene, 2387
† 2-Iodopropane, 1248

† 3-Iodopropene, 1170
2-Iodosovinyl chloride, 0687
Iodosylbenzene, 2245
Iodosylbenzene tetrafluoroborate, 2288
4-Iodosyltoluene, 2749
4-Iodotoluene, 2746
† Iodotrimethylsilane, 1302
4-Iodylanisole, 2751
Iodylbenzene, 2246
2-Iodylbenzoic acid, 2677
4-Iodyltoluene, 2750
2-Iodylvinyl chloride, 0688
Nitrogen triiodide—ammonia, 4630
Nitrogen triiodide—silver amide, 4629
Nitrogen triodide, 4628
Orthoperiodic acid, 4537
μ-OxO-*I,I*-bis(trifluoroacetato-*O*)-*I,I*-diphenyliodine (III), 3691
Oxybisphenyliodonium bistetrafluoroborate, 3468
Pentafluoroiodosylbenzene, 2051
Periodic acid, 4419
Phenyl, phenylethynyliodonium perchlorate, 3628
9-Phenyl-9-iodafluorene, 3741
Phenyliodine(III) chromate, 2240
Phenyliodine(III) nitrate, 2244
I-Phenyl-*I*-(*p*-toluenesulfonyloxy)-(2-azido-2-phenyl)vinyliodine(III), 3815
Phosphorus triiodide, 4631
Poly(dimercuryimmonium iodide hydrate), 4449
Potassium iodate, 4614
Potassium periodate, 4615
Sodium iodate, 4619
Tetrafluoroiodosyl hypofluorite, 4350
Tetraiodoarsonium tetrachloroaluminate, 0057
Tetraiododiphosphane, 4632
Tetraiodoethylene, 0982
1,1,1-Triacetoxy-1,2-benziodoxol-3-one, 3604
Trifluoroacetyliminoiodobenzene, 2898
Trifluoromethyliodine(III) isocyanate, 1042
Triiodocyclopropenium iodide, 1335
(ARYLSULFONYLIMINOIODO)BENZENES

vic-IODO-ALKOXY or -ACETOXY COMPOUNDS—C(I)—C(OR)— or —C(I)—C(OAc)—

Dimmel, D. R., *Chem. Eng. News*, 1977, **55**(27), 38

Treatment of 3,7,7-trimethylbicyclo[4.1.0]heptane (Δ3-carene) with iodine and copper acetate in methanol gave 3-iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0]heptane. A

50 g sample exploded violently after standing at ambient temperature in a closed container for 10 days. This and the corresponding iodoacetoxy compound showed large exotherms at 90°C on DTA examination, ΔH for the latter substance being calculated as 4.19 MJ/mol (13.1 kJ/g). Similar products derived from methylcyclohexene also exhibited substantial exotherms from 60°C upwards. It is recommended that *vicinal* iodo-alkoxy or -acetoxy derivatives of terpenes should be handled very cautiously.
See IODINE COMPOUNDS

ION EXCHANGE RESINS

Ammonia solution

Colman, C., *Chem. Engrg.* (New York), 1980, **87**, 274
Passage of a conc. solution of ammonia through a column of the acid form of a cation exchange resin led to a sudden neutralisation exotherm which damaged the bed, owing to its poor heat dissipation characteristics.

Dichloromethane

See Dichloromethane: Azide form of quaternary etc.

Dichromates

1. Earle, H., *Chem. & Ind.*, 1979, 391
2. Ardern, T. V., *Chem. & Ind.*, 1972, 532

The possibility is discussed of cleaning organically fouled ion exchange resins by treatment with weakly acid dichromate solutions [1]. The dangers of using separate dichromate treatment (which produces very high loading on the resin), and then mineral acid treatment, which liberates very high concentrations of chromic acid and leads to violent or explosive oxidation of the organic material (or of the resin), are stressed [2].
See Nitric acid: Ion exchange resins

Sugar solution

Colman, C., *Chem. Engrg.* (New York), 1980, **87**, 224
When passage of a sugar solution at 90°C through a weak-base anion exchange resin was interrupted, an explosion occurred. This was attributed to an exothermic Maillard reaction (interaction of an amino acid with a glycosidic OH group) under the poor heat transfer conditions in a particulate bed without fluid flow.

Water

1. Anon., *Chem. Eng. News*, 1953, **31**, 5120
2. Anon., *Chem. Eng. News*, 1948, **26**, 1480
3. *MCA Case History No. 2155*

A three-year-old sample of ion exchange resin was soaked in dilute hydrochloric acid, and then charged into a 2.5 cm diameter glass column. After soaking in distilled water for 15 min, the tube burst violently, presumably owing to swelling of the resin. Process resins as far as possible before charging into a column [1]. The earlier incident involved a column, charged with dry resin, which burst when wetted [2]. The case history involved dry resin which expanded and split a glass column when wetted with an aqueous salt solution.

IRRADIATION DECOMPOSITION INCIDENTS

1. United States Office of Nuclear Safety, NFS Safety Notice 93-01, 1993, p. 4
2. Ames Lab. Yellow Alert 970924a, Internet, 1997

Radiation breaks chemical bonds, usually cleaving molecules into small fragments, which may be gaseous and thus pressurise sealed containers. Some incidents of this type, usually involving hydrogen from water, are in this handbook. However methane and other small hydrocarbons, carbon monoxide and carbon dioxide may also be produced by degradation of organic molecules [1]. A further consequence is that molecules labelled with radio-isotopes, even tritium and carbon 14, are less stable and often more reactive than the normal molecule [2]. Several instances are recorded where the energy of activation needed to initiate decomposition of various (usually unstable) materials has been provided by radiation of various types. Such incidents may be found under the group entries and in the individual entries:

Azidoacetic acid, 0770
Benzoyl nitrate, 2685
Bis(cyclopentadienyldinitrosylchromium), 3269
* Bis(methylcyclopentadienyl)peroxoniobium chloride, 3516
Borazine, 0176
Caesium pentafluorotelluramide, 4251
Caesium tetraperchloratoiodate, 4155
* Calcium hypochlorite, 3918
† Carbon disulfide, 0557
Carbonic diazide, 0547
Chlorine dioxide, 4036
Dicyclopentadienylperoxyniobium chloride, 3265
Difluorodiazirine, 0341
1,8-Diphenyloctatetrayne, 3782
Glyceryl trinitrate, 1192
Hexaoxygen difluoride, 4321
Iodine(III) perchlorate, 4134
1-Iodo-1,3-butadiyne, 1377
Isopropyl hypochlorite, 1243
Mercury(I) cyanamide, 0520
Nitrogen (Liquid), 4730
Nitrogen trichloride, 4137
Plutonium(IV) nitrate, 4763
Potassium perchlorate, 4012
Potassium triazidocobaltate(1—), 4206
Radon, : Water, 4887
* Silver acetylide—silver nitrate, 0566
Silver azide, 0023
Trifluoromethyl hypofluorite, : Hydrocarbons, 0352

CHLOROPHYLL
DIOXYGENYL POLYFLUOROSALTS
IGNITION SOURCES
INORGANIC AZIDES

ISOCYANIDES $RN=C:$

Acids

Sidgwick, 1950, 673

Acid catalysed hydrolysis of isocyanides ('carbylamines') to primary amines and formic acid is very rapid, sometimes explosively so.

See DIISOCYANIDE LIGANDS

ISOPROPYLIDENE COMPOUNDS $Me_2C=C$

Ozone

See Ozone: Isopropylidene compounds

ISOXAZOLES

Cardillo, P., *Chim. e Ind.* (Milan), 1988, **70**(6), 90—91

After an incident involving the violent decomposition of hot 3-methyl-5-aminoisoxazole, the thermal stability of 7 other isoxazole derivatives was studied by DSC, TGA and ARC. Only 4-amino-3-isoxazolidinone decomposed exothermally in an open crucible, but all did so in sealed capsules, evolving much gas. The results below give isoxazole derivative, ARC onset temperature of decomposition (°C)/adiabatic exotherm (°C)/max. pressure (bar); and DSC heat of decomposition (kJ/g), respectively for all 9 compounds.

Isoxazole, 136/611/23, 1.36; 5-methyl-, 171/535/10, 1.08; 3,5-dimethyl-, 210/687/17, -; 3-amino-, 115/791/19, 2.67; 3-carbonamido-5-methyl-, 155/792/11, 1.22; 3-amino-5-methyl-, 140/77/above 170 (vent), 1.97; 5-amino-3-methyl-, 90/650/above 170 (vent), 1.43; 4-amino-3-isoxazolidinone, 76/647/11, 1.67; 3-phenyl-5-isoxazolone, 105°/659°/9 bar, 0.985 kJ/g.

Individual entries are:

4-Amino-3-isoxazolidinone, 1134
5-Amino-3-methylisoxazole, 1498
3-Amino-5-methylisoxazole, 1497
3-Aminoisoxazole, 1133
5-Aminoisoxazole-3-carbonamide, 1472
3,5-Dimethylisoxazole, 1882
† Isoxazole, 1107
5-Methylisoxazole, 1464
3-Phenyl-5-isoxazolone, 3116

See other GAS EVOLUTION INCIDENTS, N—O COMPOUNDS

JOJOBA WAX (Esters of $C_{20—22}$ monoene acids and alcohols)

Ozone

Zabicky, J. *et al., J. Am. Oil Chem. Soc.*, 1986, **63**, 1547—1550

The solid diozonide prepared from jojoba wax decomposed violently at 110—120°C

See other OZONIDES

KETONE PEROXIDES (See text below)

1. Davies, 1961, 72
2. Kirk-Othmer, 1967, Vol. 14, 777

The variety of peroxides (monomeric, dimeric, trimeric or polymeric) which can be produced from interaction of a given ketone and hydrogen peroxide is very wide (see type groups below for structures). The proportions of the products in the reaction mixture depend on the reaction conditions used as well as the structure of the ketone. Many of the products appear to coexist in equilibrium, and several types of structure are explosive and sensitive in varying degrees to heat and shock. Extreme caution is therefore required in handling ketone peroxides in high concentrations, particularly those derived from ketones of low MW. Acetone is thus entirely unsuitable as a reaction or cleaning solvent whenever hydrogen peroxide is used [1,2]. Relevant groups are:

Individually indexed compounds are:

Bis(2-hydroperoxy-2-butyl) peroxide, 3073
3,6-Diethyl-3,6-dimethyl-1,2,4,5,tetraoxane, 3047
3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane, 3540
3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane, 3189
3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 2512
3,6,9-Triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexoxonane, 3556
Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane, 3686

CYCLIC PEROXIDES
1-OXYPEROXY COMPOUNDS
POLYPEROXIDES

KETOXIMINOSILANES $RSi(ON{=}CMeEt)_3$

Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3

During preparation of tris(ketoximino)silanes, two violent explosions attributed to acid-catalysed exothermic rearrangement/decomposition reactions occurred. Although these silane derivatives can be distilled under reduced pressure, the presence of acidic impurities (e.g. 2-butanone oxime hydrochloride, produced during silane preparation) drastically reduces thermal stability. Iron(III) chloride at 500 ppm caused degradation to occur at 150°, and at 2% concentration violent decomposition set in at 50°C.

See 2-Butanone oxime hydrochloride

See other OXIMES

KINETICS AND INSTABILITY

Grewer, T., *DECHEMA Monograph*, 1980, 88(1818—1835), 21—30

One of the principal causes of batch chemical processes becoming unstable is the combination of a high reaction exotherm and a low reaction rate (or rates if there is more than one component reaction in the overall process). A secondary cause of reaction delay leading to instability is too little mass transfer. To permit safe operation of such reaction systems, the reaction energy (which may be expressed as a dimensionless reaction number) and the reaction rate(s) must be known. The possibility of there being a lower safe limit as well an upper safe limit to reaction temperature is discussed.

KJELDAHL METHOD

1. Beet, A. E., *J. R. Inst. Chem.*, 1955, **79**, 163, 269
2. McDonald, M. S., *Lab. Pract.*, 1979, **28**, 927
3. Pick, R. W., Internet, 1996

Possible hazards introduced by variations in experimental techniques in Kjeldahl nitrogen determination were discussed [1]. Modern variations involving use of improved catalysts and hydrogen peroxide to increase reaction rates, and of automated methods, have considerably improved safety aspects [2]. An anecdote is given of the classic technique when sodium hydroxide was to be added to the sulphuric acid digestion and was allowed to trickle down the wall of the flask. It layered over the sulphuric acid. Gentle mixing then provoked rapid reaction and a steam explosion [3].

KONDRATIEV CYCLES

Kletz, T. *Chem & Ind.*, 1999, (21), 834; *ibid.*, 2005, (11), 28

The name given to an approximately sixty year cycle perceived in economics and many other fields of human activity. Cynics have explained it as showing that humanity hastens to repeat its follies just as soon as those who were of an age to understand what went wrong last time have died or become senile. There is a similar phenomenon in industrial accidents [1], but with a cycle more like ten to twenty years. This may approximate to the average working life of a plant-trained chemist or engineer, before he is downsized, promoted to the fantasies of higher management, or leaves in pursuit of such promotion. It may be assumed that little basic understanding of any process operated more than 30 years remains active, whatever may be found in paper reports on file from its origins - look for them before trying ‘improvements’. However, computer files of twenty years of age are likely to be unreadable, even if they can still be found, since both storage media and word-processing package will be obsolete [1]. Recurrent accidents, due to forgetting a long-described hazard, also occur in academic circles.

2-Chloronitrobenzene: 2-Ethylhexylamine, 2134

See TOLLENS’ REAGENT

KRYPTON COMPOUNDS

Very few are known, all may be seen as derived from FKr^+. All are thermodynamically unstable and energetic fluorinating agents. Listed are:
Fluorohydrocyanokrypton hexafluoroarsenate, 0366
Fluorokrypton hexafluoroarsenate, 0096
Krypton difluoride, 4307
See also XENON COMPOUNDS

LAGGING

See INSULATION

LANTHANIDE IODIDE SILICIDES **MISi**

Mattausch, H. *et al., Angew. Chem. (Int.)*, 1998, **37**(4), 499

The MISi compounds of Lanthanum, Cerium and Praseodymium, and two slightly less iodinated lanthanum derivatives were prepared by fusing stoichiometric mixtures of the triiodides, the metal and silicon. They ignite violently on contact with water.

LANTHANIDE METALS

Oxidants

Bailar, 1973, Vol. 4, 70

While there are considerable variations in reactivity, several of the series of lanthanide metals ignite in halogens above 200°, in air or oxygen above 150—180°C, or lower in presence of moisture.
See Europium
See other METALS

LANTHANIDE NITROBENZOATES

1. Kurpiol-gorgol, R. *et al., Croat. Chem. Acta*, 1999, **72**(1), 77
2. Ferenc, W. *et al., Croat. Chem. Acta*, 1999, **72**(4), 779
3. Ferenc, W. *et al., ACH - Models Chem.*, 1999, **136**(5-6), 583

A series of Polish studies on substituted lanthanide (III) nitrobenzoates (which includes phthalates [1]) have found that on heating in air they first lose water of hydration, then decompose explosively at temperatures above 200°C.
See Lanthanum 2-nitrobenzoate
Scandium 3-nitrobenzoate, 3810
Yttrium 4-nitrobenzoate trihydrate, 3811
NITROARYL COMPOUNDS
See also HEAVY METAL DERIVATIVES

LANTHANIDE—TRANSITION METAL ALLOY HYDRIDES

$LaNi_5H_6$, $LaNi_{4.5}Al_{0.5}H_5$

Imamoto, T. *et al., J. Org. Chem.*, 1987, **52**, 5695

Several lanthanide—transition metal alloys ($LaNi_5$, $PrCo_5$, $SmCo_5$) readily absorb large volumes of hydrogen under mild conditions, and some of these alloy hydrides function as active hydrogenation catalysts: e.g., the title structures, which are pyrophoric in air. Analogous hydrides may be expected to behave similarly.
See HYDROGENATION CATALYSTS, PYROPHORIC MATERIALS

LASSAIGNE TEST

1. Lance, R. C. *et al., Microchem. J.*, 1975, **20**, 103—110
2. Taylor, D. A. H., *Chem. Brit.*, 1978, **14**, 70
3. Mumford, C., *Chem. Brit.*, 1978, **14**, 170
4. Ingham, P. L., *Chem. Brit.*, 1978, **14**, 326
5. Sugden, T. M. *et al., Chem. Brit.*, 1978, **14**, 326
6. Turfitt, G. E., *Chem. Brit.*, 1979, **15**, 614
7. McCulloch, A., *Chem. Brit.*, 1979, **15**, 614
8. Boulton, L. H., *Educ. Chem.*, 1973, **10**, 231
9. Guthrie, R. D. *et al., Chem. Brit.*, 1979, **15**, 614
10. Mazor, L., *Acta Chim. Acad. Sci. Hung.*, 1979, **101**, 3—6

Correspondence on safety aspects of the Lassaigne sodium fusion test [1]—[3] included a description of the use of 3 mm lengths of 2 mm sodium wire (from an enlarged die) as a convenient source of small pieces of sodium [4]. Subsequently the safer characteristics of zinc—calcium hydroxide [5], or zinc—sodium carbonate [6] fusion methods were propounded, though these methods may not always work with volatile fluoro compounds [7]. Overall advantage is claimed, however, for an oxygen combustion technique [8], using a flask fitted with a pressure-relieving (Bunsen) valve [9]. A safe development for organic compounds containing the hetero elements S, P, As, halogens and/or metals is to fuse the compound with potassium in vacuo at 300—500°C. After treating the cooled melt with ethanol and then water, normal microanalytical detection of ions can be used [10].

LEAD SALTS OF NITRO COMPOUNDS

Fogel'zang, A. E. *et al., Chem. Abs.*, 1978, **88**, 63813

The lead salts of nitromethane, mono-, di- or tri-nitrophenols burn at faster rates (up to 640-fold) than the parent compounds. Lead salts of trinitromethane, trinitrobutyric acid or dinitro-benzoic or -p-toluic acids burn at slightly faster rates (up to 10-fold) than the parent compounds.
See other HEAVY METAL DERIVATIVES

LECTURE DEMONSTRATIONS

1. Bodner, C. M., *J. Chem. Educ.*, 1985, **62**(12), 1105-1107
2. Schibeci, R. A., *Educ. Chem.*, 1988, **25**(5), 150—153

A variety of chemical lecture demonstrations involving unstable or highly reactive materials which have led to accidents are reviewed, and practical suggestions made to avoid such incidents [1]. Safety aspects are discussed and some relevant books and articles reviewed [2].

LIGHT ALLOYS

1. Anon., *Fire Prot. Assoc. J.*, 1959, (44), 28
2. Wassenhoven, J., *VDI Berichte*, 2001, 1601, 365

Experiments to determine the probability of ignition of gas or vapour by incendive sparks arising from impact of aluminium-, magnesium- and zinc-containing alloys with rusty steel are described. The risk is greatest with magnesium alloys, where the higher the magnesium content, the lower the impact energy necessary for incendive sparking. Wide ranges of ignitable gas concentrations (flammability limits) also tend to promote ignition [1].

Light metals are themselves a fire and explosion hazard as dusts or, for Mg and Ti, chips. This is illustrated by accidents which actually occurred [2].

See Iron(III) oxide: Aluminium and subsequent entries
Magnesium: Metal oxides, 4685
THERMITE REACTIONS

Water
MOLTEN METAL EXPLOSIONS

LIME FUSION

See Calcium hydroxide: Polychlorinated phenols, etc.

LINSEED OIL

FPA H90, 1980

1. Watts, B. G., private comm., 1965
2. Taradoire, F., *Rev. Prod. Chim.*, 1925, **28**, 114—115

Cloths used to apply linseed oil to laboratory benches were not burned as directed, but dropped into a waste bin. A fire developed during a few hours and destroyed the laboratory. Tests showed that heating and ignition were rapid if a draught of warm air impinged on the oil-soaked cloth. Many other incidents involving ignition of autoxidisable materials dispersed on absorbent combustible fibrous materials have been recorded [1]. Practical tests on the spontaneous combustion of cotton waste soaked in linseed oil and other paint materials had been reported 40 years previously [2].

See also INSULATION

LIQUEFIED GASES

Water

1. Urano, Y. *et al., Chem. Abs.*, 1976, **84**, 107979; 1977, 86, 108970
2. Porteous, W. M. *et al., Chem. Eng. Progr.*, 1976, **72**(5), 83—89
3. Fowles, G. R., *Science*, 1979, **204**, 168—169
4. Hixson, R. S., *Diss. Abstr. Int.*, 1981, **B41**, 3070—3078
5. Flock, R. A. *et al., Proc. Amer. Phys. Soc. Top. Conf.: Shock Waves in Condensed Matter*, 1984, 273—276

The explosive phenomena produced by contact of liquefied gases with water were studied. Chlorodifluoromethane produced explosions when the liquid—water temperature differential exceeded 92°C, and propene did so at differentials of 96—109°C. Liquid propane did, but ethylene did not, produce explosions under the conditions studied [1]. The previous literature on superheated vapour explosions has been critically reviewed, and new experimental work shows the phenomenon to be more widespread than had been thought previously. The explosions may be quite violent, and mixtures of liquefied gases may produce overpressures above 7 bar [2]. Alternative explanations involve detonation driven by phase changes [3][4] and do not involve chemical reactions. Explosive phase transitions from superheated liquid to vapour have also been induced in chlorodifluoromethane by 1.0 J pulsed ruby laser irradiation. Metastable superheated states (of 25°C) achieved lasted some 50 ms, the expected detonation pressure being 4—5 bar [5].

See LIQUEFIED NATURAL GAS, SUPERHEATED LIQUIDS, VAPOUR EXPLOSIONS

LIQUEFIED NATURAL GAS

FPA H30, 1974

Organic liquids, or Water

1. Katz, D. L. *et al., Hydrocarbon Proc.*, 1971, **50**, 240
2. Anon., *Chem. Eng. News*, 1972, **50**(8), 57
3. Yang, K., *Nature*, 1973, **243**, 221—222
4. *NFPA 59A*, Quincy (Ma), Natl. Fire Prot. Assocn., 1985

The quite loud ‘explosions’ (either immediate or delayed) which occur when LNG (containing usually high proportions of heavier materials) is spilled onto water are non-combustive and harmless [1]. Superheating and shock-wave phenomena are involved [2]. There is a similar effect when LNG of normal composition (90% methane) is spilled on to some C_5C_8 hydrocarbons or methanol, acetone or 2-butanone [3]. A US National Fire Code covers site selection, design, construction and fire prevention aspects of LNG installations [4].

See SUPERHEATED LIQUIDS

LIQUEFIED PETROLEUM GASES

1. Various authors, *J. Haz. Mat.*, 1988, **20**, 3—62
2. Anon., *Loss Prev. Bull.*, 1987, (77)
3. *NFPA 58, 59, 59A*, Quincy (Ma), Natl. Fire Prot. Assocn., 1989, 1989, 1985, resp.
4. *Institute of Petroleum Model Code of Safe Practice,* Vol 1, New York, Wiley, 1987
5. *The Storage of LPG at Fixed Installations,* Health and Safety Executive (UK), 1987
6. *The Keeping of LPG in Cylinders and Similar Containers,* Guidance Note CS4, Health and Safety Executive (UK), 1986
7. *Safe Handling of LPG* (2 videos), Inst. Chem. Eng. Rugby (UK).

Complete issues are devoted to various aspects of the fire and explosion hazards associated with bulk storage and transportation of liquefied petroleum gases, including fire exposure tests, simulation and prediction of various effects with computer programs, and preventive measures [1] and actual incidents [2]. Users should consult statutory requirements and codes of practice [3,4,5,6]. A video training package is available [7].

See also CRYOGENIC LIQUIDS, LIQUEFIED GASES, LIQUEFIED NATURAL GAS

LIQUID AIR

Liquid air, formerly used widely as a laboratory or industrial cryogenic liquid, has been involved in many violent incidents. Many of these have involved the increased content of residual liquid oxygen produced by fractional evaporation of liquid air during storage. However, liquid air (with ~30 vol% oxygen content) is still a powerful oxidant in its own right. Liquid nitrogen, now widely available, is recommended as a safer coolant than liquid air, though care is still necessary to prevent condensation of atmospheric oxygen during its use.

Carbon disulfide

Biltz, W., *Chem. Ztg.*, 1925, **49**, 1001

A mixture prepared as a cooling bath exploded violently and apparently spontaneously.

Charcoal

Taylor, J., *J. Sci. Instrum.*, 1928, **5**, 24

Accidental contact via a cracked glass trap caused a violent explosion. Nitrogen is a safer coolant.

Ether

Danckwort, P. W., *Angew. Chem.*, 1927, **40**, 1317

Addition of liquid air to ether in a dish caused a violent explosion after a short delay. Previous demonstrations had been uneventful, though it was known that such mixtures were impact- and friction-sensitive.

Hydrocarbons

McCartey, L. V. *et al., Chem. Eng. News*, 1949, **27**, 2612

All hydrocarbons (and most reducing agents) form explosive mixtures with liquid air.

See Nitrogen (Liquid)

Oxygen (Liquid), 4826

LIQUID NITROGEN COOLING

Several explosive incidents, mostly of academic origins, have appeared in which violently reactive compositions have been assembled at liquid nitrogen temperatures and then removed from the bath and allowed to warm up, in the hope of a moderated reaction. Solids do not react with each other, and solutes often crystallise on cooling, even when any solvent remains liquid, thus locally concentrating the reagents. This procedure offers scant cooling or control as solids melt and react. In the most extreme cases, one or more of the reactive, but unreacted, solids was actually a gas at ambient temperature, and rapidly resumed this state as reaction warmed it. No academic title, or degree, frees a chemist from the laws of physics – or the need to think!

Liquid nitrogen being of lower boiling point than oxygen, oxygen is inclined to condense into air-exposed cooled systems, if these also contain combustible organics, the results can be devastating.

See Lithium 3,3-dimethylbut-1-ynide
See also Oxygen (Liquid)

LITHIUM PERALKYLURANATES $Li[UR_n]$

Sigurdson, E. R. *et al., J. Chem. Soc., Dalton Trans.*, 1977, 818

In a series of solvated lithium peralkyluranate(IV) and (V) complexes, all were pyrophoric and the former type may explode unpredictably at ambient temperature.

See other HEAVY METAL DERIVATIVES, PYROPHORIC MATERIALS
See related ALKYLMETALS

LOSS PREVENTION

Often may be assumed a capitalistic euphemism for Safety; The *Journal of Loss Prevention in the Process Industries*, or the proceedings of the eponymous annual, conference will be found to concern themselves almost entirely with averting potentially deadly mishap – which will also be destructive of equipment. Little if any attention is given to avoiding the production of off-specification product, a regular and large loss to industry.

LUBRICANTS

Several incidents involving reaction of various oxidants with lubricants used in or on moving parts of chemical plant have occurred, and this possibility should be guarded against when oxidants are to be used in equipment with lubricated parts. Some incidents may be found under the entries:

Bromine trifluoride: Silicone grease, 0241
Chlorine: Silicones, 4041
Dinitrogen tetraoxide: Laboratory grease, 4720
Nitric acid: Silicone oil, 4430
Oxygen (Gas): Oil films, 4825
Sodium bromate: Grease, 0257

LYCOPODIUM POWDER

Kubala, T. A. *et al., Chem. Abs.*, 1982, **96**, 145450

In a study of discharge ignition of air suspensions of the powder, it was found that the wall layers deposited from air dispersions were as easily ignited as the dispersions.

See DUST EXPLOSION INCIDENTS (references 25,29)

MAGNETIC STIRRERS

(Editor's opinion)

The magnetic stirrer hotplates now commonly used, whereby a follower on the bottom of the reaction vessel is impelled by an electric motor beneath, are not very effective. They do not disperse explosive solids, liquids, or mixtures very well, usually leaving an annulus at the bottom. They do, however, grind this against the wall, especially when restarted after removal of the flask. Several explosions in this book seem likely to have been initiated thus. An overhead stirrer, which does not permit grinding between surfaces, is to be preferred, and generally mixes better too. Contrary to some recommendations, the magnetic stirrer is not a way to avoid ignition by sparking electric motors; it includes one and most flammable vapours are denser than air, settling downwards and not up. Probably the safest laboratory agitator is an overhead air-turbine motor, especially if run on nitrogen.

MAXIMUM REACTION HEAT

Yoshida, T., *Handbook of Hazardous Reactions with Chemicals*, Tokyo, Tokyo Fire Dept., 1980

The calculated figures for maximum reaction heat which are given throughout this text for various reactive pairs of chemicals are quoted from the extensive tables given in the above book. The figures indicate the heat release that could occur in 1 g of a binary mixture at the composition calculated to give the maximum, with the heat release in kJ and the composition in wt% of the compound against which the MRH figure is given. Most values are given in the form MRH 2.45/66, indicating that the maximum reaction heat of 2.45 kJ/g is developed for a mixture containing 66% of the component A against which the figure is quoted. In some instances the values are in the form 2.45/99+ or 2.45/tr. In the former case this implies that the component A is decomposed catalytically by traces of the other component B, and in the latter case that traces of the component A catalyse decomposition of the other component B.

The book also gives a rating of probability of ignition for each reactive pair, based on whether the energy release is above 2.9 kJ/g (Grade A, high probability), between 1.25 and 2.9 (B, medium probability), between 0.42 and 1.25 (C, low probability) or below 0.42 kJ (D, nil). Nearly 400 pages of tables of binary mixtures are given in the book, but only the figures for binary mixtures already in this Handbook for other reasons have been inserted, to permit a rough correlation to be made between the calculated figures for energy release and the physical effects in the incidents described.

MEK PEROXIDE

See Bis(2-hydroperoxy-2-butyl) peroxide

See 3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane

MERCURY COMPOUNDS

A number of mercury compounds show explosive instability or reactivity in various degrees, including the group and the individually indexed compounds:

* Acetoxydimercurio(perchloratodimercurio)ethenone, 1409
* Acetoxymercurio(perchloratomercurio)ethenone, 1408
Allylmercury(II) iodide, 1169
N,N-Bis(bromomercurio)hydrazine, 0267
N,N′-Bis(chloromercurio)hydrazine, 4058
* μ-1,2-Bis(cyanomercurio)ethanediylidenedimercury(II), 1792
* Bis(dimethylarsinyldiazomethyl)mercury, 2461
Bis(ethoxycarbonyldiazomethyl)mercury, 2973
1,2-Bis(hydroxomercurio)-1,1,2,2-bis(oxydimercurio)ethane, 0704
Bis-*N*(imidosulfurdifluoridato)mercury, 4336
* Bis(trimethylsilyl)mercury, 2589
Chloratomercurio(formyl)methylenemercury(II), 0650
Chloromercuriodiphenylgold, 3466
* Di[bis(trifluoromethyl)phosphido]mercury, 1371
Diisopentylmercury, 3362
* Dimercury dicyanide oxide, 0979
Dimethylmercury, 0903
Diphenylmercury, 3473
Dipropylmercury, 2532
2-Hydroxyethylmercury(II) nitrate, 0853
Mercury 5,5′-azotetrazolide, 0976
Mercury bis(chloroacetylide), 1352
Mercury nitride, 4610
Mercury peroxide, 4601
Mercury(I) azide, 4607
Mercury(I) bromate, 0270
Mercury(I) chlorite, 4074
Mercury(I) cyanamide, 0520
Mercury(I) fluoride, 4306
Mercury(I) hypophosphate, 4612
Mercury(I) nitrate, 4604
‘Mercury(I) oxide’, 4608
Mercury(I) thionitrosylate, 4605
Mercury(II) 5-nitrotetrazolide, 0977
Mercury(II) acetylide, 0971
Mercury(II) *aci*-dinitromethanide, 0703
Mercury(II) amide chloride, 3993
Mercury(II) azide, 4599
Mercury(II) bromate, 0269
Mercury(II) bromide, 0268
Mercury(II) chlorite, 4071
* Mercury(II) cyanate, 0973
Mercury(II) cyanide, 0972

Mercury(II) formohydroxamate, 0800
Mercury(II) fulminate, 0974
Mercury(II) iodide, 4597
Mercury(II) nitrate, 4598
Mercury(II) *N*-perchlorylbenzylamide, 3644
Mercury(II) oxalate, 0978
Mercury(II) oxide, 4600
Mercury(II) peroxybenzoate, 3630
Mercury(II) picrate, 3427
Mercury(II) sulfide, 4602
* Mercury(II) thiocyanate, 0975
2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1587
2-Naphthalenediazonium trichloromercurate, 3242
Poly(diazomethylenemercury), 0519
Poly(dimercuryimmonium hydroxide), 4416
Potassium tetracyanomercurate(II), 1791
Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide, 2164
Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2104
Tetra(3-aminopropanethiolato)trimercury perchlorate, 3576
Tetrakis(hydroxymercurio)methane, 0470
Trimercury tetraphosphide, 4611
* Tris(iodomercurio)phosphine, 4609
POLY(DIMERCURYIMMONIUM) COMPOUNDS

METAL ABIETATES

Anon., *Fire Prot. Assoc. J.*, 1958, 255

Aluminium, calcium, cobalt, lead, manganese, sodium and zinc abietates (‘resinates’), when finely divided are subject to spontaneous heating and ignition. Store in sealed metal containers away from fire hazards.

Individually indexed compounds are:
  Aluminium abietate, 3911
  Calcium abietate, 3894
  Lead abietate, 3896
  Manganese abietate, 3895
  Sodium abietate, 3799
  Zinc abietate, 3897

See other SELF-HEATING AND IGNITION INCIDENTS

METAL ACETYLIDES $C{\equiv}CM$

1. Brameld, V. F. *et al., J. Soc. Chem. Ind.*, 1947, **66**, 346
2. Houben-Weyl, 1970, Vol. 13.1, 739
3. Rutledge, 1968, 85—86
4. Miller, 1965, Vol. 1, 486

5. Dolgopolskii, I. M. *et al., Chem. Abs.*, 1947, **41**, 6721
6. Roger, E. C. *et al., Inorg. Chim. Acta*, 1984, **90**(3), L47—L49
7. Köhn, J., *Chem. Abs.*, 1986, **104**, 212405

Previous literature on formation of various types of copper acetylides is discussed and the mechanism of their formation is examined, with experimental detail. Whenever a copper or copper-rich alloy is likely to come into contact with atmospheres containing [1] ammonia, water vapour and acetylene, or [2] lime-sludge, water vapour and acetylene, or a combination of these two, there is the probability of acetylide formation and danger of explosion. The action is aided by the presence of air, or air with carbon dioxide, and hindered by the presence of nitrogen. Explosive acetylides may be formed on copper or brasses containing more than 50% copper when these are exposed to acetylene atmospheres. The acetylides produced by action of acetylene on ammoniacal or alkaline solutions of copper(II) salts are more explosive than those from the corresponding copper(I) salts [1]. The hydrated forms are less explosive than the anhydrous material [2].

Catalytic forms of copper, mercury and silver acetylides, supported on alumina, carbon or silica and used for polymerisation of alkanes, are relatively stable [3]. In contact with acetylene, silver and mercury salts will also give explosive acetylides, the mercury derivatives being complex [4]. Many of the metal acetylides react violently with oxidants. Impact sensitivities of the dry copper derivatives of acetylene, buten-3-yne and 1,3-hexadien-5-yne were determined as 2.4, 2.4 and 4.0 kg m, respectively. The copper derivative of a polyacetylene mixture generated by low-temperature polymerisation of acetylene detonated under 1.2 kg m impact. Sensitivities were much lower for the moist compounds [5]. Explosive copper and silver derivatives give non-explosive complexes with trimethyl-, tributyl- or triphenyl-phosphine [6]. Formation of silver acetylide on silver-containing solders needs higher acetylene and ammonia concentrations than for formation of copper acetylide. Acetylides are always formed on brass and copper or on silver-containing solders in an atmosphere of acetylene derived from calcium carbide (and which contains traces of phosphine). Silver acetylide is a more efficient explosion initiator than copper acetylide [7].

Individually indexed compounds in this often dangerously explosive class are:

* Acetylenebis(triethyllead), 3665
* Acetylenebis(triethyltin), 3666
Barium acetylide, 0572
* Bis(dimethylthallium)acetylide, 2514
3-Buten-1-ynyldiethylaluminium, 3012
3-Buten-1-ynyldiisobutylaluminium, 3543
3-Buten-1-ynyltriethyllead, 3351
* 1-Butoxyethyl 3-trimethylplumbylpropiolate, 3546
Caesium acetylide, 0611
Calcium acetylide, 0582
Copper 1,3,5-octatrien-7-ynide, 3697
Copper(I) benzene-1,4-bis(ethynide), 3230
Copper(II) acetylide, 0612
Dicopper(I) 1,5-hexadiynide, 2158

Dicopper(I) acetylide, 0616
Dimethyl-1-propynylthallium, 1932
Dimethyl(phenylethynyl)thallium, 3292
Gold(I) acetylide, 0570
Lithium 1-heptynide, 2830
* Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide, 1814
Lithium acetylide, 0988
Lithium bromoacetylide, 0577
Lithium chloroacetylide, 0596
Lithium trifluoropropynide, 1043
Manganese(II) bis(acetylide), 1392
Mercury bis(chloroacetylide), 1352
Mercury(II) acetylide, 0971
3-Methyl-3-buten-1-ynyltriethyllead, 3407
Monocaesium acetylide, 0657
Monolithium acetylide, 0669
* Monolithium acetylide—ammonia, 0670
Monopotassium acetylide, 0667
Monorubidium acetylide, 0681
Monosilver acetylide, 0646
Monosodium acetylide, 0680
1,3-Pentadiyn-1-ylcopper, 1813
1,3-Pentadiyn-1-ylsilver, 1809
Potassium acetylide, 0983
1-Propynylcopper(I), 1095
Rubidium acetylide, 1021
Silver 1,3,5-hexatrienide, 2046
Silver 3-hydroxypropynide, 1085
Silver acetylide, 0565
* Silver acetylide—silver nitrate, 0566
Silver buten-3-ynide, 1404
* Silver chloroacetylide, 0563
Silver cyclopropylacetylide, 1832
Sodium acetylide, 1018
Sodium bromoacetylide, 0578
Sodium chloroacetylide, 0598
Sodium ethoxyacetylide, 1474
Sodium methoxyacetylide, 1120
Sodium phenylacetylide, 2906
Strontium acetylide, 1022
Tetraethynylgermanium, 2890
Tetraethynyltin, 2896
Thallium(I) iodacetylide, 0980
* Tributyl(phenylethynyl)lead, 3805

Triethynylaluminium, 2088
Triethynylantimony, 2118
* Triethynylarsine, 2089
See other ACETYLENIC COMPOUNDS

METAL ALKOXIDES $M(OR)_n$

1. *Alkali and Alkali-Earth Metal Alkoxides*, Brochure, Troisdorf-Oberlaar, Dynamit Nobel AG, 1974
2. Hopper, S. P. *et al., Synth. React. Inorg. Metal-Org Chem.*, 1977, **7**, 162; *J. Organomet. Chem.*, 1977, **134**, 178
3. Mebarek, A. *et al., J. Therm. Anal. & Calorimetry*, 2003, **74**(1), 293

An appendix to the brochure is devoted to safe handling of the alkoxides indicated by a suffixed asterisk in the list below, and not all of which are represented as indexed entries with page numbers. These materials are readily hydrolysed and the exotherm may ignite the solids in presence of moist air, the potassium derivatives being the most reactive. This tendency is increased by acidic conditions, and combustion of solids spreads rapidly. Potassium *tert*-butoxide is especially reactive towards a range of liquids and solvent vapours [1]. Heating of sodium methoxide, ethoxide or potassium *tert*-butoxide (at 100°C) must always be under nitrogen to prevent ignition, which occurs in presence of air, especially if moist [2]. A warning is given that, since stoichiometric reaction of alcohols with alkali metals goes nowhere near completion, a serious exotherm with gas evolution from renewed and vigorous reaction, will result on adding more alcohol (or, worse, water) to the attempt [3].

Individually indexed compounds are:

Aluminium isopropoxide, 3210
* Bis(2,4-pentanedionato)chromium, 3320
Dicyclopentadienylchromium: Alcohols, 3267
Molybdenum hexamethoxide, 2592
Potassium *tert*-butoxide, 1645
Potassium ethoxide, 0857
Potassium methoxide, 0449
* Potassium methylselenide, 0450
Rhenium hexamethoxide, 2599
* Sodium 2,2,2-trifluoroethoxide, 0701
Sodium ethoxide, 0874
Sodium isopropoxide, 1266
Sodium methoxide, 0463
* Tetrakis(butylthio)uranium, 3725
* Tetrakis(ethylthio)uranium, 3090
Titanium butoxide, 3724
Titanium tetraisopropoxide, 3573
Titanium(III) methoxide, 1313
Tungsten hexamethoxide, 2600
Zinc ethoxide, 1698

See Potassium *tert*-butoxide: Acids, or Reactive solvents

METAL AMIDOSULFATES H_2NSO_2OM

Metal nitrates or nitrites

Heubel, J. *et al., Compt. rend. [3]*, 1963, **257**, 684

Heating mixtures of barium, potassium or sodium amidosulfates or amidosulfuric acid, with sodium or potassium nitrates or nitrites, leads to reactions which may be explosive. TGA plots are given.

Individually indexed compounds are:

Barium amidosulfate, 0209
Potassium amidosulfate, 4451
Sodium amidosulfate, 4461
See other N—S COMPOUNDS

METAL AZIDE HALIDES MXN_3

Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 243

Metal halides and halogen azides react to give a range of metal azide halides, many of which are explosive. Individually indexed compounds are:

Azidopentafluorotungsten, 4352
Chromyl azide chloride, 3962
Diamminedichloroaminotrichloroplatinum(IV), 4173
Molybdenum azide tribromide, 0287
Molybdenum diazide tetrachloride, 4158
Silver azide chloride, 0009
Tin azide trichloride, 4140
Titanium azide trichloride, 4141
Titanium diazide dibromide, 0272
Tungsten azide pentabromide, 0296
Tungsten azide pentachloride, 4176
Uranium azide pentachloride, 4175
Vanadium azide tetrachloride, 4160
Vanadyl azide dichloride, 4084
See AMMINEMETAL AZIDES

METAL AZIDES MN_3

1. Mellor, 1940, Vol. 8, Suppl. 2, 16—54
2. *Energetic Materials*, Fair, H. D. and Walker, R. F. (Eds.), Vols. 1 and 2, New York, Plenum, 1977

This large and well documented group of explosive compounds contains some which are widely used industrially [1]. The text gives a thorough treatment of all aspects of the physics and chemistry (Vol. 1) and of the applications (Vol. 2) of this important group of energetic compounds [2] and individually indexed compounds are:

Aluminium azide, 0082
* Azidogermane, 4410
Barium azide, 0214
* Bis(2-aminoethyl)aminecobalt(III) azide, 1769
* Bis(cyclopentadienyl)tungsten diazide oxide, 3279

* Bis(cyclopentadienyl)vanadium diazide, 3280
Cadmium azide, 3951
Caesium azide, 4256
Calcium azide, 3930
Cerium azide, 3960
* Chromyl azide, 4233
Cobalt(II) azide, 4210
Copper(I) azide, 4281
Copper(II) azide, 4274
* Copper(II) azide hydroxide, 4264
* Diazido-bis(1,2-diaminoethane)ruthenium(II) hexafluorophosphate, 1783
* Dicarbonylmolybdenum diazide, 0991
* Dicarbonyltungsten diazide, 1009
* Dicarbonyl-π-cycloheptatrienyltungsten azide, 3117
* Dodecamethyltetraplatinum(IV) azide, 3584
* Hydrogen hexaazidothallate(III), 4497
Lead (II) azide, 4776
* Lead(IV) acetate azide, 2396
Lead(IV) azide, 4784
Lithium azide, 4680
* Lithium hexaazidocuprate(4—), 4272
* Lithium tetraazidoaluminate, 0081
Magnesium azide, 4689
* Manganese diazide hydroxide, 4427
* Manganese(III) azide, 4697
Mercury(I) azide, 4607
Mercury(II) azide, 4599
* Methylcadmium azide, 0430
Nickel azide, 4771
Palladium(II) azide, 4777
* Pentaammineazidoruthenium(III) chloride, 4067
* Phenylthallium diazide, 2279
* Poly(dimercuryimmonium azide), 4606
Potassium azide, 4647
* Potassium azidopentacyanocobaltate(3—), 1803
* Potassium hexaazidoplatinate(IV), 4660
* Potassium triazidocobaltate(1—), 4206
Silver azide, 0023
Sodium azide, 4753
Sodium triazidoaurate(?), 0113
Strontium azide, 4779
* Tetraamminecopper(II) azide, 4271
* *trans*-Tetraamminediazidocobalt(III) *trans*-diamminetetraazidocobaltate(1—), 4214
* Tetramethylammonium azidocyanatoiodate(I), 2000
* Tetramethylammonium azidocyanoiodate(I), 1999

* Tetramethylammonium azidoselenocyanatoiodate(I), 2001
Tetramethyldigold diazide, 1733
Thallium(I) azide, 4760
* Thallium(I) tetraazidothallate, 4786
Zinc azide, 4780

Acids

The majority of the metal azides are sensitive explosives and exposure to heat, friction or impact is usually undesirable. Contact of most azides, particularly readily soluble ones, with acids will produce hydrogen azide, itself an explosive and highly toxic low-boiling liquid. In presence of heavy metals, it may give other equally hazardous heavy metal azides. These may also be formed from contact of soluble azides with heavy metals.

See Hydrogen azide

Halogenated solvents

Bretherick, L., *Chem. & Ind.*, 1986, 729; *Chem. Eng. News*, 1986, **64**(51), 2

Attention is drawn to the possibility of slow formation of explosive organic azides from long contact of halogenated solvents with metal azides.

See Dichloromethane: Azide form

Relevant group entries are:
AMMINEMETAL AZIDES
AZIDE COMPLEXES OF COBALT(III)
SODIUM TETRAAZIDOMETALLATES

METAL AZOTETRAZOLIDES

Reddy, G. O. *et al., Thermochim. Acta*, 1983, **66**, 231—244

Of the four salts with Hg^{2+}, Pb^{2+}, Ba^{2+} and $2Na^{+}$, the thermal sensitivity and impact-, friction- and static spark-sensitivities decreased in that order, as expected.

These and other entries are:
Barium 5,5′-azotetrazolide, 0574
Disodium 5,5′-azotetrazolide, 1014
* Disodium 5,5′-azoxytetrazolide, 1015
Lead 5,5′-azotetrazolide, 1016
Mercury 5,5′-azotetrazolide, 0976
See other TETRAZOLES

METAL CHLORATES $M(ClO_3)_n$

NSC 371, 1977

Individually indexed compounds are:
Aluminium chlorate, 0065
Barium chlorate, 0205
Cadmium chlorate, 3946
Chloric acid, 3990

Lead(II) chlorate, 4099
Magnesium chlorate, 4077
Manganese(II) chlorate, 4081
Potassium chlorate, 4011
Silver chlorate, 0011
Sodium chlorate, 4033
Zinc chlorate, 4100

See other METAL HALOGENATES

Acids

1. Mellor, 1941, Vol. 2, 315
2. Stossel, E. *et al.*, US Pat. 2 338 268, 1944

In addition to being oxidants in contact with strong acids, metal chlorates liberate explosive chlorine dioxide gas. With conc. sulfuric acid, a violent explosion may occur unless effective cooling is used [1]. Heating a moist mixture of a metal chlorate and a dibasic organic acid (tartaric or citric acid) liberates chlorine dioxide diluted with carbon dioxide [2].

Ammonium salts

Mixtures are incompatible.

See Ammonium chlorate

Phosphorus, or Sugar, or Sulfur

1. Black, H. K., *School Sci. Rev.*, 1963, **44**(53), 462
2. *59th Ann. Rep. HM Insp. Explos. (Cmd. 4934)*, 5, London, HMSO, 1934
3. Berger, A., *Arbeits-Schutz.*, 1934, **2**, 20
4. Taradoire, F., *Chem. Abs.*, 1938, **32**, 1455_6

The extremely hazardous nature of mixtures of metal chlorates with phosphorus, sugar or sulfur, sometimes with addition of permanganates and metal powders, frequently prepared as amateur fireworks, is stressed. Apart from being powerfully explosive, such mixtures are dangerously sensitive to friction or shock, and spontaneous ignition sometimes occurs [1]. Chlorates containing 1—2% of bromates or sulfur as impurities are liable to spontaneous explosion [3]. The danger of mixtures of chlorates with sulfur or phosphorus is such that their preparation without a Home Office licence was prohibited in the UK by Orders in Council over 50 years ago [2]. Mixtures of sulfur with lead, silver, potassium or barium chlorates ignited at 63—67, 74, 160—162 and 108—111°C, respectively [4].

Sulfur, Initiators

1. Taradoire, F., *Bull. Soc. Chim. Fr.*, 1942, **9**, 610—620
2. Ellern, 1968, 304
3. Chapman, D. *et al., J. Pyrotech.*, 1997, (6), 30
4. Chapman, D. *et al., J. Pyrotech.*, 2000, (11), 16

The effect of initiators (diluted sulfuric acid, chlorine dioxide, sulfur dioxide or disulfur dichloride) on ignition of mixtures of barium, lead or potassium chlorates with sulfur was examined [1]. Presence of copper ion or metal (e.g. from a sieve) may also lead to explosion of such mixtures [2]. A review of hazards of sulphur/chlorate mixtures in the firework industry has been published [3]. Dilution does little to reduce thermal sensitivity. Iron adds impact sensitivity to the habitual frictional initiation [4].

METAL CYANATES $M(N:C:O)_n$

1. Singmaster, J. A., *Chem. Eng. News*, 1985, **63**(7), 2
2. Pilznienski, J. F., *Chem. Eng. News*, 1985, **63**(16), 2
3. Weast, 1979, D-67—D-79

Disregarding the differences in structure, it was argued that because the empirical formulae of fulminate and cyanate ions are identical, metal cyanates are likely to be as unstable as metal fulminates [1]. The results of practical tests, in which samples of various metal cyanates were heated in a flame, coupled with long industrial experience of the use of molten salt process baths containing over 40% of cyanates, show that the assumption on explosive instability of metal cyanates is not warranted [2]. The observation that silver or copper(II) cyanates burned smoothly on exposure to flame [2] suggests that the explosion recorded for silver cyanate (*ibid.*) may have involved close confinement or other unusual conditions during heating. Although mercury(II) cyanate (*ibid.*) vapourised gradually and completely without flaming on heating [2], two incidents of explosion during grinding or crushing operations have been recorded. The unusual tendency for many derivatives of silver and mercury to decompose forcefully (with separation of the metal, rather than the oxide as with other metals), suggests that other metal cyanates are likely to be rather more stable. This view is supported by available thermodynamic data [3], which show that while several cyanides are endothermic compounds, the few cyanates for which figures are quoted are all exothermic compounds and unlikely to be intrinsically unstable. A few reports of mishap could involve hydrolysis of the cyanate, liberating ammonia, followed by formation of “fulminating” noble metals.

See Mercury(II) cyanate, Potassium cyanate, Silver cyanate
See also FULMINATING METALS

METAL CYANIDES(AND CYANO COMPLEXES) $M(CN)_n$, $[M(CN)_n]$

1. von Schwartz, 1918, 399, 327; Pieters, 1957, 30
2. *Res. Rept. No. 2*. New York, Nat. Board Fire Underwriters, 1950

Several members of this (often endothermic) group of compounds which contain heavy metals tend to explosive instability, and most are capable of violent oxidation under appropriate circumstances. Fusion of mixtures of metal cyanides with metal chlorates, perchlorates, nitrates or nitrites causes a violent explosion [1]. Addition of one solid component (even as a residue in small amount) to another molten component is also highly dangerous [2]. Individually indexed compounds are:

* Ammonium hexacyanoferrate(II), 2572
* Barium thiocyanate, 0573
* μ-1,2-Bis(cyanomercurio)ethanediylidenedimercury(II), 1792
Cadmium cyanide, 0585
* Chromyl isocyanate, 0610
* Chromyl isothiocyanate, 0609
Copper(I) cyanide, 0617

Copper(II) cyanide, 0613
Copper(II) thiocyanate, 0615
* Dimercury dicyanide oxide, 0979
Gold(I) cyanide, 0307
Iron(III) hexacyanoferrate(4—), 3733
Lead(II) cyanide, 0995
* Lead(II) thiocyanate, 0996
* Lithium thiocyanate, 0529
* Mercury(II) cyanate, 0973
Mercury(II) cyanide, 0972
* Mercury(II) thiocyanate, 0975
Nickel(II) cyanide, 0993
* Potassium azidopentacyanocobaltate(3—), 1803
Potassium cyanide, 0523
Potassium hexacyanoferrate(II), 2057
Potassium hexacyanoferrate(III), 2056
Potassium octacyanodicobaltate(8—), 2875
* Potassium tetracyanomercurate(II), 1791
Potassium tetracyanotitanate(IV), 1794
* Potassium thiocyanate, 0526
* Silver cyanate, 0299
Silver cyanide, 0298
Sodium cyanide, 0533
* Sodium pentacyanonitrosylferrate(2—), 1807
* Sodium tetracyanatopalladate(II), 1796
* Sodium thiocyanate, 0535
Zinc cyanide, 1000
See also METAL THIOCYANATES, MOLTEN SALT BATHS

METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

Although the C-F bond is a stronger than average single covalent bond, the extreme electronegativity of fluorine makes the formation of ionic fluorides far more favourable thermodynamically. The stability of organofluorine compounds is therefore largely kinetic. Although metallated organofluorine derivatives can often be isolated they are far from thermodynamically stable and may show it. Alkoxides derived from fluorinated alcohols and phenols have also exploded. Such compounds should be treated with caution if isolated and are best handled in solution. Salts of fluorinated acids are certainly more stable and have not yet been reported as giving trouble. The metals involved are usually lithium and aluminium, but cadmium, sodium, magnesium and zirconium also feature and the thermodynamic situation changes little, whatever the metal.

Bis(trifluoromethyl)cadmium, 0583
1-*tert*-Butyl-3-(*N*-*tert*-butyl-2-lithaminoethyl)imidazol-2-ylidene, 3612
Caesium cyanomethylbis(trifluoromethyl)hydroxyborate, 1405
Caesium dodecakistrifluoromethylcarba-*closo*-dodecaborate, 3589

Dicyclopentadienylpentafluorophenylcerium, 3689
Dicyclopentadienyltrifluoromethyltitanium(1+) fluoride, 3388
[1,1′-Oxybis[ethane]]tris(pentafluorophenyl)aluminium, 3823
Pentafluorophenyllithium, 2052
Sodium tris(η^4 naphthalene)tantalate(1-), 3869
Tris(pentafluorophenyl)aluminium, 3731
Tris(pentafluorophenyl)boron, 3732
See Pentafluoroethyllithium
See also Sodium: Fluorinated alkanols
See FLUORINATED ORGANOLITHIUM COMPOUNDS

N-METAL DERIVATIVES N—M

Many metal derivatives of nitrogenous systems containing one or more bonds linking nitrogen to a metal (usually, but not exclusively, a heavy metal) show explosive instability. Individually indexed compounds are:

* Amminebarium bis(nitrophenylide), 3512
Amminepentahydroxyplatinum, 4566
Ammonium nitridoosmate, 4518
Antimony(III) nitride, 4724
Barium nitride, 0219
Barium nitridoosmate, 0213
Barium *N*-perchlorylbenzylamide, 3642
Barium perchlorylamide, 0203
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-*N*3,*N*5]-(T-4) cobalt, 3862
N,N-Bis(bromomercurio)hydrazine, 0267
N,N′-Bis(chloromercurio)hydrazine, 4058
Bis(dihydroxygold)imide, 0114
Bis(dimethylamino)dimethylstannane, 2593
Bismuth amide oxide, 0229
Bismuth nitride, 0230
cis-Bis(trimethylsilylamino)tellurium tetrafluoride, 2611
Cadmium amide, 3948
Cadmium nitride, 3954
Caesium amide, 4254
Caesium nitride, 4260
Caesium pentafluorotelluramide, 4251
Calcium cyanamide, 0315
Calcium nitride, 3940
Cerium nitride, 3959
Chromium nitride, 4231
Cobalt(III) amide, 4195
Cobalt(III) nitride, 4208
Copper bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3855
Copper(I) nitride, 4283
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1425

Diamminedihydroxyosmium, 4567
* Dibutylthallium isocyanate, 3187
Dilithium 1,1-bis(trimethylsilyl)hydrazide, 2591
* Dipyridinesodium, 3274
Disilver cyanamide, 0304
Disodium *N,N′*-dimethoxysulfonyldiamide, 0907
Germanium imide, 4408
Gold(I) nitride—ammonia, 0117
Gold(III) nitride trihydrate, 0118
* Hexaamminecalcium, 3927
Hexafluoroisopropylideneaminolithium, 1049
* Hydrogen hexaazidothallate(III), 4497
Lead bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3856
Lead nitride, 4748
Lead(II) imide, 4433
Lithium amide, 4456
Lithium bis(trimethylsilyl)amide, 2590
Lithium diethylamide, 1680
Lithium nitride, 4681
Lithium triethylsilylamide, 2573
Magnesium nitride, 4693
Mercury nitride, 4610
Mercury(I) cyanamide, 0520
Mercury(II) amide chloride, 3993
Mercury(II) *N*-perchlorylbenzylamide, 3644
Monopotassium perchlorylamide, 3988
Nitrogen triiodide—silver amide, 4629
Nitrosylruthenium trichloride, 4138
Pentaamminedinitrogenruthenium(II) salts, 4591
Pentakis(dimethylamino)tantalum, 3378
Pentasilver diamidophosphate, 0046
Pentasilver orthodiamidophosphate, 0044
Plutonium nitride, 4721
Poly(dimercuryimmonium hydroxide), 4416
* Poly(disilicon nitride), 4752
Potassium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide, 4667
Potassium amide, 4450
Potassium diethylamide, 1679
* Potassium dinitrogentris(trimethylphosphine)cobaltate(1—), 3222
Potassium methylamide, 0471
Potassium nitride, 4666
Potassium nitridoosmate, 4646
Potassium perchlorylamide, 4013
Potassium sulfurdiimidate, 4659
Potassium thiazate, 4643
Potassium triamidothallate ammoniate, 4546

Rhenium nitride tetrafluoride, 4338
Rubidium nitride, 4722
* Seleninyl bis(dimethylamide), 1752
Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide, 0039
Silver 5-aminotetrazolide, 0391
Silver amide, 0015
Silver hexanitrodiphenylamide, 3423
Silver imide, 0030
Silver nitride, 0038
Silver *N*-nitrosulfuric diamidate, 0016
Silver *N*-perchlorylbenzylamide, 2730
Silver tetrazolide, 0365
3-Sodio-5-(5′-nitro-2′-furfurylideneamino)imidazolidin-2,4-dione, 2903
Sodium 5-azidotetrazolide, 0548
Sodium amide, 4459
Sodium diethylamide, 1682
Sodium hydrazide, 4495
Sodium *N*-chlorobenzenesulfonamide, 2222
Sodium nitride, 4718
Sodium tetrasulfur pentanitridate, 4769
* Sodium triammine, 4576
Tetrakis(dimethylamino)titanium, 3098
* Tetramethylammonium amide, 1776
* Tetraselenium tetranitride, 4765
Tetrasilver diimidodioxosulfate, 0043
Tetrasilver diimidotriphosphate, 0042
Tetrasilver orthodiamidophosphate, 0041
* Tetratellurium tetranitride, 4767
Thallium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3-5-triide, 4756
Thallium(I) nitride, 4726
N,N,4-Trilithioaniline, 2173
Tris(dimethylamino)antimony, 2594
Trisilver tetranitride, 0040
Tris(thionitrosyl)thallium, 4759
Trithorium tetranitride, 4768
Uranium(III) nitride, 4727
Zinc bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3857
Zinc dihydrazide, 4558
Zirconium nitride, 4728
See METAL AZIDE HALIDES, METAL AZIDES, METAL HYDRAZIDES, NITRIDES, PERCHLORYLAMIDE SALTS

METAL DUSTS

1. Jacobson, M. *et al., Rept. Invest. 6516(9)*, Washington, US Bur. Mines, 1961
2. Brown, H. R., *Chem. Eng. News*, 1956, **34**, 87

3. Nedin, V. V. *et al., Chem. Abs.*, 1972, **77**, 167636—167641
4. Martin, R., *Powder. Metall.*, 1976, **19**, 70—73
5. Alekseev, A. G. *et al., Chem. Abs.*, 1977, **86**, 175311
6. Hulanichi, S. *et al., Chem. Abs.*, 1977, **87**, 87208
7. Popov, E. I. *et al., Chem. Abs.*, 1981, **94**, 194483
8. Cashdollar, K. L., *Proc. Safety Progress*, 1994, **13**(3) 139.
9. Schulz, W. D., *Korrosion* (Dresden), 1986, **17620(1)**, 42—44
10. Burachonok, I. N., *Chem. Abs.*, 1987, **107**, 12139
11. Boiko, V. M. *et al., Arch. Combust.*, 1988, **8**(2), 101
12. Gieras, M. *et al., Arch. Combust. 1997*, 17(1-4), 145
13. Ivanov, G. *et al., NATO Sci. Ser. 1*, 1999, **26**, 341

Of the 313 samples examined, the dust explosion hazards of finely divided aluminium, aluminium—magnesium alloys, magnesium, thorium, titanium and uranium, and the hydrides of thorium and uranium, are rated highest [1]. The need to exercise caution when handling dusts of some recently introduced reactive metals was discussed briefly. Some form explosive mixtures, not only with air or oxygen, but also with nitrogen and carbon dioxide, reacting to give the nitride or carbonate. Intimate mixtures with generally non-oxidising oxosalts may also be explosive. Beryllium, cerium, germanium, hafnium, lithium, niobium, potassium, sodium, thorium, titanium, uranium and zirconium are discussed [2]. The pyrophoric capabilities of titanium and titanium—aluminium alloys were studied, the effect of particle size on flammability and explosion parameters of aluminium and magnesium powders dispersed in air was determined, and explosion hazards of aluminium, magnesium and aluminium-based alloy powders and use of inert gas media as preventives were assessed. In a study to determine explosivity of ferrochromium, ferromanganese, ferrosilicon, ferrotitanium, manganese and calcium—silicon powders, the latter proved to be the most active [3]. Metal dust and powder explosion risks were reviewed [4], including those during spraying operations in powder production [5]. Self-ignition characteristics and explosibility parameters were determined for dusts of aluminium, lead, magnesium, zinc and aluminium—magnesium alloys [6]. More accurate results (higher values) in determination of lower concentration limit for metal dusts are obtained in a conical explosion chamber [7]. Dust explosion studies (temperature, pressure, influence of particle size) on Mg, Al, Ti, Cr, Fe, Nb, Sn, Hf, Ta, W and the non-metals B, C, Si & S are reported. Under the conditions of test, Cu, Mo, Ni and Pb were not flammable [8]. Possible reasons for an explosion in a plant using acetylene—oxygen flame spraying of aluminium, tin—lead, or zinc were analysed [9]. The relationship between particle size of tool steel powders from machining operations and ignition temperatures in air suspensions or as a bed are expressed by two equations [10]. A study of ignition of metal powders in reflected shock waves is reported [11]. A study of lanthanide metal dust explosion, with especial reference to nitrogen/water atmospheres [12]. Metal dusts generated by passing large electric currents through metal wires or foils in an inert atmosphere are of exceptional activity due to structural stresses. Even normally unreactive metals, such as copper, may show low auto-ignition temperatures [13].

Relevant group entries are:
FERROALLOY POWDERS
FINELY DIVIDED METALS
THERMITE REACTIONS

METAL FIRES

Mellottee, H., *Rév. Gen. Therm., (Fr)*, 1977,**16**, 523—538

Methods of extinguishing different types of metal fires are reviewed, with 86 references.

METAL FULMINATES **MC≡N→O**

1. Urbanski, 1967, Vol. 3, 157
2. Hackspill, L. *et al., Chem. Abs.*, 1938, **32**, 4377a

The metal fulminates are all powerfully explosive. Of several salts examined, those of cadmium, copper and silver were more powerful detonators than mercury fulminate, while thallium fulminate was much more sensitive to heating and impact. Formally related salts are also explosive [1]. Sodium, potassium, rubidium and caesium fulminates are all easily detonated by feeble friction or heat. They all form double salts with mercury(II) fulminate which also explode readily, that of the rubidium salt at 45°C [2].

Individually indexed compounds are:
Cadmium fulminate, 0586
Copper(II) fulminate, 0614
* Dimethylthallium fulminate, 1207
Mercury(II) fulminate, 0974
Silver fulminate, 0300
Sodium fulminate, 0534
Thallium fulminate, 0536
* Tripropyllead fulminate, 3357

METAL HALIDES **MX_n**

Members of this group have often featured as secondary reagents in hazardous combinations of chemicals. Individually indexed compounds are:
Aluminium bromide, 0060
Aluminium chloride, 0062
Aluminium iodide, 0079
Americium trichloride, 0090
* Ammonium bromide, 0251
* Ammonium chloride, 3995
* Ammonium fluoride, 4293
* Ammonium iodide, 4507
Antimony pentachloride, 4178
Antimony trichloride, 4151
* Antimony trichloride oxide, 4144
* Antimony(III) chloride oxide, 4035

Beryllium chloride, 0221
Beryllium fluoride, 0223
* Bis(1-chloroethylthallium chloride) oxide, 1586
Bismuth pentafluoride, 0227
* *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2611
Caesium fluoride, 4249
Calcium bromide, 0262
Calcium chloride, 3917
* Chloriminovanadium trichloride, 4159
* Chlorogermane, 3986
Chromium pentafluoride, 4220
Chromium(II) chloride, 4046
Chromium(III) chloride, 4121
* Chromyl chloride, 4048
Cobalt trifluoride, 4194
Cobalt(II) bromide, 0263
Cobalt(II) chloride, 4042
Cobalt(III) chloride, 3793
Copper(I) bromide, 0264
Copper(I) chloride, 4050
* Dibromogermane, 0266
Germanium tetrachloride, 4156
Gold(III) chloride, 0111
Indium bromide, 0288
Iridium hexafluoride, 4356
Iron(II) bromide, 0265
Iron(II) chloride, 4055
Iron(II) iodide, 4389
Iron(III) bromide, 0285
Iron(III) chloride, 4127
Lead chloride, 4106
Lead tetrachloride, 4166
Lead(II) fluoride, 4323
Magnesium chloride, 4075
* Manganese dichloride dioxide, 4080
* Manganese fluoride trioxide, 4295
Manganese tetrafluoride, 4337
* Manganese trichloride oxide, 4135
Manganese trifluoride, 4329
Manganese(II) chloride, 4079
Mercury(I) fluoride, 4306
Mercury(II) bromide, 0268
Mercury(II) iodide, 4597
Molybdenum hexafluoride, 4359
Molybdenum pentachloride, 4174
Neptunium hexafluoride, 4360

Osmium hexafluoride, 4364
Palladium tetrafluoride, 4341
Palladium trifluoride, 4335
* Pentaamminechlororuthenium chloride, 4131
* Phenylvanadium(V) dichloride oxide, 2239
Platinum hexafluoride, 4365
Platinum tetrafluoride, 4342
Plutonium hexafluoride, 4366
Potassium chloride, 4009
* Potassium heptafluorotantalate(V), 4373
* Potassium hexafluoromanganate(IV), 4357
Potassium iodide, 4613
* Rhenium chloride trioxide, 4039
Rhenium hexafluoride, 4367
* Rhenium nitride tetrafluoride, 4338
* Rhenium tetrachloride oxide, 4161
Rhodium tetrafluoride, 4343
Rhodium(III) chloride, 4149
Ruthenium(III) chloride, 4150
Silver chloride, 0008
Silver difluoride, 0014
Silver fluoride, 0013
Sodium chloride, 4030
Sodium iodide, 4618
Tantalum pentachloride, 4179
Tellurium tetrabromide, 0295
Thallium, 4916
Tin(II) chloride, 4064
Tin(II) fluoride, 4325
Tin(IV) chloride, 4168
Titanium dibromide, 0283
Titanium diiodide, 4625
Titanium tetrachloride, 4170
Titanium tetraiodide, 4633
Titanium trichloride, 4152
Titanium(II) chloride, 4111
* Triethoxydialuminium tribromide, 2550
* Triethyldialuminium trichloride, 2551
Trirhenium nonachloride, 4190
Tungsten dichloride, 4113
Tungsten diiodide, 4626
Tungsten hexachloride, 4187
* Tungsten tetrabromide oxide, 0293
Uranium hexachloride, 4186

Uranium hexafluoride, 4369
Vanadium dichloride, 4112
* Vanadium tribromide oxide, 0291
Vanadium trichloride, 4153
* Vanadium trichloride oxide, 4145
Zinc chloride, 4114
Zinc iodide, 4627
Zirconium dibromide, 0284
Zirconium tetrachloride, 4172
Zirconium tetraiodide, 4634
Zirconium trichloride, 4154
Zirconium(II) chloride, 4115
See also METAL PNICTIDES

METAL—HALOCARBON INCIDENTS

1. Lenze, F. *et al., Z. Ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 255, 293, 337, 373; *Chem. Ztg.*, 1932, **56**, 921—923
2. Artz, G. D. *et al., Sensitivity of Metal—Halogenated Solvent Combinations*, Rept. AD665057, Richmond (Va.), USNTIS, 1968
3. Cutler, D. P., *J. Haz. Mat.*, 1987, **17**(1), 99—108
4. U.S. Dept of Energy, 1994, HDBK-1081-94, (*Spontaneous Heating and Pyrophoricity*), 51

Various combinations of alkali- and alkaline earth-metals with halocarbon solvents were found to be highly heat- or impact-sensitive explosives [1]. Many combinations of more recently introduced metals with halocarbons have since been found hazardous, and the results of impact-testing of combinations of 9 powdered metals with 7 solvents are tabulated. Barium shavings showed the highest sensitivity [2]. Hazardous reactions of light metals (aluminium, magnesium, lithium, sodium, potassium) wuth halogenated hydrocarbons and polymers are reviewed, with 81 references [3]. Although largely a rehash of an earlier paper, a report describes several incidents in which carbon tetrachloride has contributed to ignition or explosion of zirconium, barium, sodium, uranium and plutonium [4].

Some examples of relevant incidents are:
Barium, : Halocarbons, 0200
Beryllium, : Halocarbons, 0220
† Bromomethane, : Metals, 0428
Chloroform, : Metals, 0371
Plutonium, : Carbon tetrachloride, 4882
Samarium, : 1,1,2-Trichlorotrifluoroethane, 4905
Tin, : Carbon tetrachloride, Water, 4906
Titanium, : Halocarbons, 4913
Uranium, : Carbon tetrachloride, 4917
Zirconium, : Carbon tetrachloride, 4922
See also HALOCARBONS: Metals

METAL HALOGENATES $M(XO_3)_n$

Individually indexed compounds are:

Barium bromate, 0202
Barium iodate, 0211
Bromic acid, 0248
Lead bromate, 0277
Mercury(I) bromate, 0270
Potassium iodate, 4614
Silver iodate, 0020
Sodium iodate, 4619
Zinc bromate, 0278

See other METAL OXOHALOGENATES

Metals and oxidisable derivatives, or Non-metals, or Oxidisable materials

1. Mellor, 1946, Vol. 2, 310; 1956, Vol. 2, Suppl. 1, 583—584; 1941, Vol. 3, 651
2. von Schwartz, 1918, 323

Intimate mixtures of chlorates, bromates or iodates of barium, cadmium, calcium, magnesium, potassium, sodium or zinc, with finely divided aluminium, arsenic, copper; carbon, phosphorus, sulfur; hydrides of alkali- and alkaline earth-metals; sulfides of antimony, arsenic, copper or tin; metal cyanides, thiocyanates; or impure manganese dioxide may react violently or explosively, either spontaneously (especially in presence of moisture) or on initiation by heat, friction, impact, sparks or addition of sulfuric acid [1]. Mixtures of sodium or potassium chlorate with sulfur or phosphorus are rated as being exceptionally dangerous on frictional initiation.

See METAL CHLORATES

METAL HYDRAZIDES $M^{n+}(HN^{-}—NH_2)_n$

Hydrazine and its Derivatives, Schmidt, F. W., New York, Wiley, 1984, 371

This class of compounds has been little studied as they tend to explode during preparation and isolation. There are entries for:

Calcium hydrazide, 3926
Lithium hydrazide, 4491
Sodium hydrazide, 4495

See also *N*-METAL DERIVATIVES

METAL HYDRIDES MH_n, $[MH_n]$

1. Banus, M. D., *Chem. Eng. News*, 1954, **32**, 2424—2427
2. Mackay, 1966, 66
3. *Metal Hydrides*, Müller, W. M. *et al.*, New York, Academic Press, 1968
4. Hariguchi, S. *et al., Chem. Abs.*, 1981, **94**, 159191
5. Vogman. L. P., *Chem. Abs.*, 1984, **101**, 116147
6. Klusever, P. A. A. *et al., Angew. Chem. (Intern. Ed.)*, 1986, **25**, 465

Precautions necessary for safe handling of three main groups of hydrides of commercial significance were discussed. The first group (sodium hydride, lithium or sodium tetrahydroaluminates) ignite or explode in contact with liquid water or high humidity, while the second group (lithium, calcium, strontium or barium hydrides; sodium or potassium tetrahydroborates) do not. Burning sodium hydride is reactive enough to explode with the combined water in concrete. The 3rd group ('alloy' or non-stoicheiometric hydrides of titanium, zirconium, thorium, uranium, vanadium, tantalum, and palladium) are produced commercially in very finely divided form. Though less pyrophoric than the corresponding powdered metals, once burning is established they are difficult to extinguish, and water-, carbon dioxide- or halocarbon-based extinguishers caused violent explosions. Powdered dolomite is usually effective in smothering such fires [1]. The trihydrides of the lanthanoid (rare earth) metals are pyrophoric in air and the dihydrides, though less reactive, must be handled under inert atmosphere [2]. A later reference states that finely divided metal hydrides of the second group (lithium, calcium, barium and strontium hydrides) will ignite in air or react violently, sometimes explosively, with water or air of high humidity [3]. In an examination of the lower concentration limits, explosion pressures and pressure-increase rates of a series of mixed metal hydride powders dispersed in air, hydrides of MgNi were the most hazardous [4]. The minimum oxygen concentrations for explosion of most volatile hydrides of group IIIA—VA elements is nearly zero, so complete exclusion of air is essential for safe working. Presence of impurities in hydride mixtures increases the risk of ignition [5]. A new method of producing alkali-metal hydrides involves hydrogenation of butyllithium, butylsodium or butylpotassium in hexane—tetramethylethylenediamine. The hydrides so produced are superactive with a wide range of materials, and of course immediately pyrophoric in air [6].

Individually indexed compounds of this group of active reducants are:

∗ Aluminium hydride—diethyl ether, 0073
∗ Aluminium hydride—trimethylamine, 0072
∗ Azidogermane, 4410
Barium hydride, 0207
Beryllium hydride, 0224
∗ Bromogermane, 0246
Cadmium hydride, 3947
Caesium hydride, 4252
Calcium hydride, 3921
Cerium dihydride, 3956
Cerium trihydride, 3957
∗ Chlorogermane, 3986
Copper(I) hydride, 4280
∗ Dibromogermane, 0266
Digallane, 4404
† Digermane, 4414
† Germane, 4411
† Hydrogen telluride, 4482
Lanthanum dihydride, 4455
Lanthanum hydride, 4490
∗ Lithium diphenylhydridotungstate(2—), 3497
Lithium hydride, 4426
Magnesium hydride, 4457

Magnesium—nickel hydride, 4458
Plutonium(III) hydride, 4504
Poly(germanium dihydride), 4409
Poly(germanium monohydride), 4407
Potassium hydride, 4421
Rubidium hydride, 4444
Sodium hydride, 4438
† Stibine, 4505
Thorium dihydride, 4483
Thorium hydride, 4535
Titanium dihydride, 4484
Titanium—zirconium hydride, 4485
Trigermane, 4415
Uranium(III) hydride, 4506
Uranium(IV) hydride, 4536
Zinc hydride, 4486
'Zirconium hydride', 4487

See COMPLEX HYDRIDES, PYROPHORIC MATERIALS
See entry LANTHANIDE—TRANSITION METAL ALLOY HYDRIDES

METAL HYPOCHLORITES $M(OCl)_n$

A widely used group of industrial oxidants which has been involved in numerous incidents, some with nitrogenous materials leading to formation of nitrogen trichloride. and the individually indexed compounds:

Calcium hypochlorite, 3918
Lead(II) hypochlorite, 4092
Magnesium hypochlorite, 4076
Sodium hypochlorite, 4031

See Chlorine: Nitrogen compounds
See BLEACHING POWDER

Amines

Kirk-Othmer, 1963, Vol. 2, 104

Primary or secondary amines react with sodium or calcium hypochlorites to give *N*-chloroamines, some of which are explosive when isolated. Application of other chlorinating agents to amines or their precursors may also produce the same result under appropriate conditions.

See other METAL OXOHALOGENATES
See related HYPOHALITES

METALLURGICAL SAMPLE PREPARATION

Standard methods of preparing samples for metallurgical examination sometimes involve extremely hazardous combinations of oxidants, such as nitric or perchloric acid, and organic solvents. These are frequently destabilised by metal catalysis. Resultant incidents will be recorded under the entry for the oxidant in question.

METAL NITRATES **$M(NO_3)_n$**

Individually indexed compounds are:

- * Ammonium hexanitrocerate, 3958
- * Ammonium nitrate, 4517
- Barium nitrate, 0212
- Caesium nitrate, 4255
- Calcium nitrate, 3929
- * Chromyl nitrate, 4232
- Cobalt(II) nitrate, 4209
- * Copper(II) glycinate nitrate, 0901
- Copper(II) nitrate, 4273
- * Dimethyltin dinitrate, 0910
- * Heptasilver nitrate octaoxide, 0047
- * 2-Hydroxyethylmercury(II) nitrate, 0853
- Iron(III) nitrate, 4391
- Lead(II) nitrate, 4744
- Lithium nitrate, 4679
- Magnesium nitrate, 4688
- Manganese(II) nitrate, 4696
- Mercury(I) nitrate, 4604
- Mercury(II) nitrate, 4598
- * 2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1587
- Nickel(II) nitrate, 3583
- Plutonium(IV) nitrate, 4763
- Potassium nitrate, 4645
- Silver nitrate, 0022
- Sodium hexaoxodinitrate, 4735
- Sodium nitrate, 4716
- Sodium pentaoxodinitrate, 4734
- Sodium tetraoxodinitrate, 4733
- Sodium trioxodinitrate, 4732
- * Tetrahydroxotritin(2+) nitrate, 4520
- Thallium(III) nitrate, 4757
- Tin(II) nitrate, 4745
- * Triethylphosphinegold nitrate, 2553
- Uranyl nitrate, 4747
- * Vanadium trinitrate oxide, 4758
- Zinc nitrate, 4746

See MOLTEN SALT BATHS
See other METAL OXO-NONMETALLATES

Aluminium
See Aluminium: Metal nitrates, etc.

Citric acid
Shannon, I. R., *Chem. & Ind.*, 1970, 149

During vacuum evaporation of an aqueous mixture of unspecified mixed metal nitrates and citric acid, the amorphous solid exploded when nearly dry. This was attributed to oxidation of the organic residue by the nitrates present, possibly catalysed by one of the oxides expected to be produced.

Esters, or Phosphorus, or Tin(II) chloride

Pieters, 1957, 30

Mixtures of metal nitrates with alkyl esters may explode, owing to formation of alkyl nitrates. Mixtures of a nitrate with phosphorus, tin(II) chloride or other reducing agents (i.e. redox combinations) may react explosively.

See other REDOX REACTIONS

Ethanol

Pitwell, L. R., *Chem. Eng. News*, 1978, **56**(37), 56

In the analysis of water, the use of ethanol to remove more than traces of nitrate or nitrite ion may lead to formation of fulminic acid, and if mercury(II) is used as a catalyst, explosive mercury fulminate may be formed.

Silver nitrate: Ethanol, 0022

See Mercury(II) nitrate: Ethanol

Metal phosphinates

1. Mellor, 1940, Vol. 8, 881
2. Costa, R. L., *Chem. Eng. News*, 1947, **25**, 3177

Mixtures of metal nitrates and phosphinates, previously proposed as explosives [1], explode on heating.

Organic matter

1. Bowen, H. J. M., *Anal. Chem.*, 1968, **40**, 969; private comm., 1968
2. Grewelling, T., *Anal., Chem.*, 1969, **41**, 540—541
3. Crutchfield, C. A. *et al., J. Chem. Ed.*, 1991, **68**(7), 620
4. Editor's comments
5. Scheepers, P. *et al., South African Pat.* 98 03, 403

When organic matter is destroyed for residue analysis by heating with equimolar potassium nitrate—sodium nitrate mixture to 390°C, a 20-fold excess of nitrate must be used. If over 10% of organic matter is present, pyrotechnic reactions occur which could be explosive [1]. Subsequent to an explosion while a citric acid—sodium nitrate mixture was being heated at below 500°C, experiments on the effect of heating various organic materials with metal nitrates showed the tendency for explosion to increase from magnesium through calcium to sodium nitrate. This is in the order of m.p. of the nitrates, and explosion may occur when the nitrates melt and make intimate contact with the organic matter. Pretreatment with nitric acid may reduce the explosion risk [2]. A slurry of nickel nitrate, starch, an amine and some presumably inert components proved to be a deflagrating explosive when cyclone dried, igniting above 135°C. Caution is advised when mixing nitrates with oxidisable materials [3]. Nanotechnologists have described various methods of making micro-particles of (usually) transition metal oxides by pyrolysis of organic salts of those metals, sometimes admittedly mixed with the nitrates, on other occcasions prepared from them by ion exchange, without actually removing the exchanged nitrate prior to pyrolysis; this is usually violent and seems destined to remain a nano-technique.

Recent accidents suggest that the scientific world needs to be reminded that for the first 500 years of firearms and the first 300 of civil blasting the only explosive available was a mixture of one of the more stable and less oxidising metal nitrates with not very combustible carbonaceous material plus a catalyst. Gunpowder has been largely replaced by safer and more reliable explosives, but similar mixes remain unsafe because potentially explosive, especially if the mixing is at the molecular level in a complex. Substitutes for gunpowder are occasionally patented, they often consist of a carbohydrate and a metal nitrate [5]. It cannot always be assumed that the safety of metal nitrates is the greater when they are hydrated [4].

See Citric acid, above

See also Copper(II) nitrate

Potassium hexanitrocobaltate

See Potassium hexanitrocobaltate(3—)

Vinyl sulphones

See VINYL SULPHOXIDES

METAL NITRITES $M(NO_2)_n$

Individually indexed compounds are:

Magnesium nitrite, 4687
* Nitritonitrosylnickel, 4737
* Potassium hexanitrocobaltate(3—), 4207
Potassium nitrite, 4644
Sodium nitrite, 4715

See MOLTEN SALT BATHS

See other METAL OXONON-METALLATES, OXIDANTS

Metal Cyanides

See Sodium nitrite: Metal cyanides

Nitrogenous bases

Metal nitrites react with salts of nitrogenous bases to give the corresponding nitrite salts, many of which are unstable.

See NITRITE SALTS OF NITROGENOUS BASES

Potassium hexanitrocobaltate

See Potassium hexanitrocobaltate(3—)

METAL NITROPHENOXIDES $O_2NC_6H_4OM$

Author's comments, 1988

Several metal salts of nitrophenols exhibit very limited thermal stability, especially heavy metal salts, and several instances of explosive decomposition at modest (or even ambient) temperatures have been recorded. Individual entries are:

* Cobalt(II) picramate, 3454
Lead 2,4,6-trinitroresorcinoxide, 2064
* Lead 2-amino-4,6-dinitrophenoxide, 3462
* Lithium 4-nitrothiophenoxide, 2170
Manganese picrate hydroxide, 3736
Nickel 2,4-dinitrophenoxide hydroxide, 3739
Nickel 2-nitrophenoxide, 3458
4-Nitrophenol, : Potassium hydroxide, 2260
Potassium 4-nitrophenoxide, 2167
Silver 2-azido-4,6-dinitrophenoxide, 2068
* Silver 4-nitrophenoxide, 2119
Sodium 2,4-dinitrophenoxide, 2108
* Sodium 2-nitrothiophenoxide, 2175
Sodium 4-nitrophenoxide, 2176
Sodium picrate, 2079
Thallium(I) 2- or 4-nitrophenoxide, 2179
See PICRATES

METAL NON-METALLIDES M—E

This class includes the products of combination of metals and non-metals except C (as acetylene), H, N, O, and S, which are separately treated in the groups below.

Individually indexed compounds are:

Aluminium carbide, 1027
Aluminium phosphide, 0083
Bismuth nitride, 0230
Caesium graphite, 2877
Calcium disilicide, 3938
Calcium phosphide, 3941
Calcium silicide, 3937
Copper diphosphide, 4278
Copper monophosphide, 4277
Copper(II) phosphide, 4284
Dialuminium octavanadium tridecasilicide, 0088
Dicobalt boride, 0128
Ditungsten carbide, 0561
* Ferrosilicon, 4384
Hexalithium disilicide, 4684
Iron carbide, 0364

Lanthanum carbide, 0987
Lead pentaphosphide, 4875
Lithium heptapotassium di(tetrasilicide), 4671
Lithium tripotassium tetrasilicide, 4670
Magnesium boride, 0168
Magnesium nitride, 4693
Magnesium phosphide, 4694
Magnesium silicide, 4692
Manganese phosphide, 4706
Manganese(II) telluride, 4703
Platinum diarsenide, 0107
Potassium graphite, 3101
Potassium silicide, 4653
Rubidium graphite, 3104
Sodium phosphide, 4809
Sodium silicide, 4795
* Tetraamminelithium dihydrogenphosphide, 4590
Thorium dicarbide, 1023
Titanium carbide, 0558
Trimercury tetraphosphide, 4611
Tungsten carbide, 0560
Uranium carbide, 0559
Uranium dicarbide, 1024
Zinc phosphide, 4870
Zirconium dicarbide, 1025

METAL ACETYLIDES
N-METAL DERIVATIVES
METAL HYDRIDES
METAL OXIDES
METAL SULFIDES
NITRIDES
See also METAL PNICTIDES

Water

Many metal non-metallides react with water to evolve highly volatile, toxic, highly flammable even pyrophoric, hydrides of the non-metal. Even more react with acid similarly.

METAL OXALATES $(MOCO.-)_2$

Mellor, 1941, Vol. 1, 706

The tendency for explosive decomposition of heavy metal oxalates is related to the value of the heat of decomposition.

Individually entries are:

Copper(I) oxalate, 0619
Iron(III) oxalate, 2058

Mercury(II) oxalate, 0978
* Potassium dinitrooxalatoplatinate(2—), 0984
Silver oxalate, 0569

See other HEAVY METAL DERIVATIVES

METAL OXIDES MO_n

Malinin, G. V. *et al., Russ. Chem. Rev.*, 1975, **44**, 392—397

Thermal decomposition of metal oxides was reviewed. Some oxides (cobalt(II, III) oxide, copper(II) oxide, lead(II, IV) oxide, uranium dioxide, triuranium octaoxide) liberate quite a high proportion of atomic oxygen, with a correspondingly higher potential for oxidation of fuels than molecular oxygen.

This large group covers a wide range of types of reactivity and there is a separate entry for the related group:

METAL PEROXIDES

Individually indexed compounds are:

Aluminium oxide, 0087
* Antimony trichloride oxide, 4144
* Antimony(III) chloride oxide, 4035
Antimony(III) oxide, 4845
Barium oxide, 0215
Beryllium oxide, 0225
* Bis(1-chloroethylthallium chloride) oxide, 1586
Bismuth trioxide, 0233
* Bis(trimethylsilyl) chromate, 2587
Cadmium oxide, 3952
Caesium oxide, 4258
Caesium trioxide, 4257
Calcium oxide, 3931
Chromium trioxide, 4236
Chromium(II) oxide, 4235
Chromium(III) oxide, 4245
Cobalt(II) oxide, 4211
Cobalt(III) oxide, 4215
Copper(I) oxide, 4282
Copper(II) oxide, 4275
Dibismuth dichromium nonaoxide, 0232
Dilead(II)lead(IV) oxide, 4855
Disilver pentatin undecaoxide, 0036
Gallium(I) oxide, 4405
Indium(II) oxide, 4636
Iridium(IV) oxide, 4639
Iron(II) oxide, 4392
Iron(II,III) oxide, 4399
Iron(III) oxide, 4397
Lanthanum oxide, 4674

Lead(II) oxide, 4818
Lead(IV) oxide, 4828
Magnesium oxide, 4690
* Manganese chloride trioxide, 4016
* Manganese dichloride dioxide, 4080
* Manganese fluoride trioxide, 4295
* Manganese trichloride oxide, 4135
Manganese(II) oxide, 4699
Manganese(IV) oxide, 4700
Manganese(VII) oxide, 4704
'Mercury(I) oxide', 4608
Mercury(II) oxide, 4600
Molybdenum(IV) oxide, 4711
Molybdenum(VI) oxide, 4712
Nickel(II) oxide, 4815
Nickel(III) oxide, 4817
Nickel(IV) oxide, 4816
Niobium(V) oxide, 4812
Osmium(IV) oxide, 4827
Osmium(VIII) oxide, 4852
Palladium(II) oxide, 4819
Palladium(III) oxide, 4842
Palladium(IV) oxide, 4829
* Phenyliodine(III) chromate, 2240
Platinum(IV) oxide, 4830
* Potassium dioxide, 4651
* Potassium trioxide, 4652
* Rhenium chloride trioxide, 4039
* Rhenium tetrachloride oxide, 4161
Ruthenium(VIII) oxide, 4856
* Selenium dioxide, 4832
Silver(I) oxide, 0032
Silver(II) oxide, 0025
* Sodium dioxide, 4793
Sodium oxide, 4796
* Sodium trioxide, 4794
Tantalum(V) oxide, 4859
Thallium(III) oxide, 4848
* Thorium oxide sulfide, 4820
Tin(II) oxide, 4823
Tin(IV) oxide, 4834
Titanium(IV) oxide, 4836
Triuranium octaoxide, 4865
Tungsten(IV) oxide, 4838
Tungsten(VI) oxide, 4850
* Undecaamminetetraruthenium dodecaoxide, 4593

Uranium(IV) oxide, 4837
* Vanadium trichloride oxide, 4145
Vanadium(III) oxide, 4849
Vanadium(V) oxide, 4860
Zinc oxide, 4824
* Zirconium oxide sulfide, 4821

METAL OXOHALOGENATES MXO_n

Solymosi, F., *Acta Phys. Chem.*, 1976, **22**, 75—115

This class covers the four levels of oxidation represented in the series hypochlorite, chlorite, chlorate and perchlorate, and as expected, the oxidising power of the anion is roughly proportional to the oxygen content, though stability factors are also important. The class has been subdivided under the group headings below, each of which has its own listing of member compounds.

Some individually indexed compounds are:

* Ammonium iodate, 4508
* Ammonium periodate, 4509
Cadmium chlorate, 3946
Calcium chlorite, 3919
* Lead acetate—lead bromate, 1535
Lead(II) chlorite, 4096
Mercury(II) bromate, 0269
Potassium bromate, 0255
Potassium chlorate, 4011
Potassium periodate, 4615
Silver bromate, 0007
Sodium bromate, 0257
Sodium chlorite, 4032
Thallium bromate, 0260

CHLORITE SALTS
METAL HALOGENATES
METAL HYPOCHLORITES
METAL PERCHLORATES

METAL OXOMETALLATES $M^+ MO_n^-$

Salts with oxometallate anions function as oxidants, those with oxygen present as peroxo groups being naturally the more powerful, and separately grouped.

Individually indexed oxometallate salts are:

* Bis(benzene)chromium dichromate, 3845
Calcium chromate, 3920
Copper chromate oxide, 4217
Dibismuth dichromium nonaoxide, 0232
Lead chromate, 4237
Lithium chromate, 4230
Magnesium permanganate, 4686

Potassium dichromate, 4242
Potassium permanganate, 4642
Sodium dichromate, 4244
Sodium molybdate, 4708
Sodium permanganate, 4698
Zinc permanganate, 4705
PEROXOACID SALTS

METAL OXONON-METALLATES $M^+ EO_n^-$

This large and commonly used class of salts covers a wide range of oxidising potential. Among the more powerful oxidants are those grouped for which separate entries emphasise the individual features. Some less highly oxidised anions function as reducants which also have a separate entry. Individually indexed entries are:

* Ammonium iron(III) sulfate, 4387
* Ammonium sulfate, 4569
Barium sulfate, 0217
Calcium sulfate, 3933
Chromium(II) sulfate, 4238
Copper(II) phosphinate, 4266
Copper(II) sulfate, 4276
Iron(II) sulfate, 4393
Lead sulfate, 4854
Lithium carbonate, 0530
Lithium dithionite, 4682
Magnesium carbonate hydroxide, 0531
Magnesium nitrate, 4688
Magnesium nitrite, 4687
Magnesium sulfate, 4691
Potassium carbonate, 0528
Potassium nitrite, 4644
Silver hyponitrite, 0031
Sodium acetate, 0775
Sodium carbonate, 0549
Sodium disulfite, 4802
Sodium dithionite, 4801
Sodium hydrogen carbonate, 0389
Sodium hydrogen sulfate, 4440
Sodium metasilicate, 4799
Sodium nitrite, 4715
Sodium sulfate, 4800
* Sodium tetraborate, 0185
Sodium thiosulfate, 4798
METAL AMIDOSULFATES
METAL NITRATES
METAL NITRITES

METAL OXOHALOGENATES
METAL SULFATES
PEROXOACID SALTS

METAL PERCHLORATES $M(ClO_4)_n$

1. Burton, M., *Chem. Eng. News*, 1970, **48**(51), 55
2. Cook, R. E. *et al., J. Chem. Res.*, 1982, (S) 267; (M) 2772—2783

Though metal perbromates and periodates are known (but not perfluorates), the perchlorates have most frequently been involved in hazardous incidents over a long period. These usually stable salts are powerful oxidants and contact with combustible materials or reducants must be under controlled conditions. A severe restriction on the use of metal perchlorates in laboratory work has been recommended [1]. Attention has been drawn, on the basis of experience with cobalt(II) perchlorate, to the possibility of stable hydrated metal perchlorates being converted by unintentional dehydration to unstable (endothermic) lower hydrates capable of explosive decomposition in absence of impurities. Great care to avoid dehydration (or desolvation) is urged [2].

Individually indexed metal perchlorates are:

† Acetonitrile, : Lanthanide perchlorate, 0755
∗ Acetoxydimercurio(perchloratodimercurio)ethenone, 1409
∗ Acetoxymercurio(perchloratomercurio)ethenone, 1408
Aluminium perchlorate, 0066
∗ Antimony(III) oxide perchlorate, 4040
Barium perchlorate, 0206
∗ (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2610
Beryllium perchlorate, 0222
∗ 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate, 1583
Chromium(III) perchlorate . 6dimethyl sulfoxide, 4124
∗ Chromyl perchlorate, 4049
Cobalt(II) perchlorate hydrates, 4045
Copper(I) perchlorate, 4052
Copper(II) perchlorate, 4051
∗ Cyclopentadiene—silver perchlorate, 1853
∗ Diethylthallium perchlorate, 1676
∗ Dodecamethyltetraplatinum(IV) perchlorate, 3581
Dysprosium perchlorate, 4125
Erbium perchlorate, 4126
∗ Ethylphenylthallium(III) acetate perchlorate, 3296
Gallium perchlorate, 4129
Indium(I) perchlorate, 4008
Iron(II) perchlorate, 4056
Iron(III) perchlorate, 4056
Lead perchlorate, 4102
Lithium perchlorate, 4015

Magnesium perchlorate, 4078
Manganese(II) perchlorate, 1779
Mercury(II) perchlorate, 4072
Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide, 4073
* Methylmercury perchlorate, 0432
Neodymium perchlorate . 2acetonitrile, 4142
Nickel perchlorate, 4063
* Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3772
Potassium perchlorate, 4012
Silver perchlorate, 0012
Sodium perchlorate, 4034
* Tetrasulfurtetraimide—silver perchlorate, 0029
Tetrazirconium tetraoxide hydrogen nonaperchlorate, 4189
Tin(II) perchlorate, 4103
Titanium tetraperchlorate, 4164
Uranyl perchlorate, 4105
Vanadyl perchlorate, 4146

See SOLVATED OXOSALT INCIDENTS
See other METAL OXOHALOGENATES

Calcium hydride

Mellor, 1941, Vol. 3, 651

Rubbing a mixture of calcium (or strontium) hydride with a metal perchlorate in a mortar causes a violent explosion.

See other REDOX REACTIONS

Organic ligands

Nair, M. R. G. *et al., Talanta*, 1981, **28**, 395—396

A safe method for decomposing complexes of various organic ligands with metal perchlorates prior to analysis involves heating them with ammonium chloride, but this method should be tested on the small scale when applied to complexes not previously decomposed in this way.

See AMMINEMETAL OXOSALTS

Sulfuric acid

Pieters, 1957, 30; Schumacher, 1960, 190

Metal perchlorates with highly concentrated or anhydrous acid form the explosively unstable anhydrous perchloric acid.

See Perchloric acid: Dehydrating agents

Trifluoromethanesulfonic acid

See Trifluoromethanesulfonic acid: Perchlorate salts

METAL PEROXIDES **$M(O_2)_n$**

1. Castrantas, 1965, 1,4
2. Bailar, 1973, Vol. 2, 784

This group contains many powerful oxidants, the most common being sodium peroxide. Undoubtedly one of the most hazardous is potassium dioxide or superoxide, readily formed on exposure of the metal to air (but as the monovalent O_2^- ion it is not a true peroxide). Many transition metal peroxides are dangerously explosive. Individually indexed peroxides are:

Barium peroxide, 0216
Calcium peroxide, 3932
Mercury peroxide, 4601
* Oxodiperoxomolybdenum—hexamethylphosphoramide, 4713
* Potassium dioxide, 4651
Potassium peroxide, 4661
* Potassium trioxide, 4652
Silver peroxide, 0033
* Sodium dioxide, 4793
Sodium peroxide, 4797
* Sodium trioxide, 4794
Strontium peroxide, 4835
Zinc peroxide, 4839
See also AMMINECHROMIUM PEROXOCOMPLEXES

METAL PEROXOMOLYBDATES $M_2^+ [Mo(O_2)_4]^{2-}$

See other PEROXOMOLYBDATES AND TUNGSTATES

METAL PHOSPHINATES $M[OP(:O)H_2]_n$

This is a group of powerful reducants, several of which are of rather limited stability. Individually indexed compounds are:

Aluminium phosphinate, 0078
Barium phosphinate, 0210
Calcium phosphinate, 3925
Copper(II) phosphinate, 4266
Dipotassium phosphinate, 4425
Iron(III) phosphinate, 4388
Lead(II) phosphinate, 4526
Magnesium phosphinate, 4512
Manganese(II) phosphinate, 4514
Potassium phosphinate, 4453
Silver phosphinate, 0017
Sodium phosphinate, 4467
See other REDUCANTS

METAL PHOSPHORUS TRISULFIDES M_3PS_3

Clement, R. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 1566

When very finely divided metals (iron, manganese, nickel or zinc) are heated with elemental phosphorus and sulfur in evacuated ampoules to form the title compounds, explosions may occur, even at temperatures as low as 150—200°C.

METAL PICRAMATES $H_2N(O_2N)_2C_6H_2OM$

Srivastava, R. S. *et al., Chem. Abs.*, 1979, **91**, 76315

Explosive properties of palladium(II) and uranyl picramates were determined.

See other HEAVY METAL DERIVATIVES, POLYNITROARYL COMPOUNDS

METAL PNICTIDES

Preparative hazard

1. Hector, A. L. *et al., Z. Naturforsch. B: Chem. Sci.*, 1994, **49**(4), 477
2. Hector, A. *et al., J. Mater. Sci. Lett.*, 1994, **13**(1), 1
3. Hector, A. *et al., Polyhedron*, 1995, **14**(7), 913

(No, the editor did not know what this name meant either.) It means salts of the trivalent anions of Group V, restricted in [1] to arsenides, antimonides and bismuthides and prepared by reaction of sodium pnictides with anhydrous halides of transition and lanthanide metals. This violently exothermic reaction may initiate as low as 25°C. Avoidance of hydrated halides is cautioned since these are likely to react uncontrollably on mixing. Another paper includes a similar reaction of phosphides, initiated by grinding [2]. Nitrides are reported made from the thermally initiated reaction of sodium azide with metal halides, a very large sealed ampoule is counselled to contain the nitrogen [3].

See Sodium azide

See METAL NON-METALLIDES

See also METAL HALIDES, METATHESIS REACTIONS

METAL POLYHALOHALOGENATES $M^+ [XX'_n]$

Organic solvents, or Water

1. Whitney, E. D. *et al., J. Amer. Chem. Soc.*, 1964, **86**, 2583
2. Sharpe, A. G. *et al., J. Chem. Soc.*, 1948, 2135

Potassium, rubidium and caesium tetrafluorochlorates and hexafluorobromates react violently with water, and explosively with common organic solvents, like the parent halogen fluorides [1]. Silver and barium tetrafluorobromates ignite in contact with ether, acetone, dioxane and petrol [2]. Individual entries are:

Barium tetrafluorobromate, 0201
Caesium hexafluorobromate, 0236
Caesium tetrafluorochlorate(1—), 3963
Potassium hexafluorobromate, 0244
Potassium tetrafluorochlorate(1—), 3978
Rubidium hexafluorobromate, 0245
Rubidium tetrafluorochlorate(1—), 3982
Silver tetrafluorobromate, 0006

METAL PYRUVATE NITROPHENYLHYDRAZONES $MOCO.CC(Me)=NNHC_6H_4NO_2$

Ragno, M., *Gazz. Chim. Ital.*, 1945, **75**, 186—192

A wide range of the title salts of mono-, di- and tri-valent metals, with an *o*-, *m*- or *p*-nitro group present showed unstable or explosive behaviour on heating. The lead salt exploded violently at 240°C, while the aluminium, beryllium and silver salts are only feebly explosive.

See other NITROARYL COMPOUNDS

METALS M

Individually indexed metals are:

Aluminium, 0048
Antimony, 4901
Barium, 0200
Beryllium, 0220
Bismuth, 0226
Cadmium, 3943
Caesium, 4248
Calcium, 3916
Cerium, 3955
Chromium, 4216
Cobalt, 4193
Copper, 4261
Europium, 4286
Gallium, 4400
Germanium, 4406
Gold, 0110
Hafnium, 4594
Indium, 3579
Iridium, 4638
Lanthanum, 4672
Lead, 4876
Lithium, 4675
Magnesium, 4685
Manganese, 4695
Mercury, 4595
Molybdenum, 4707
Neodymium, 4813
Nickel, 4814
Niobium, 4811
Osmium, 4867
Palladium, 4879
Platinum, 4881
Plutonium, 4882
Potassium, 4640
Praseodymium, 4880
Rhenium, 4884
Rhodium, 4886
Rubidium, 4883
Ruthenium, 4888

Samarium, 4905
* Selenium, 4902
* Silicon, 4903
Silver, 0001
Sodium, 4790
Strontium, 4907
Tantalum, 4908
Technetium, 4909
* Tellurium, 4910
Thallium, 4916
Thorium, 4911
Tin, 4906
Titanium, 4913
Tungsten, 4919
Uranium, 4917
Vanadium, 4918
Zinc, 4921
Zirconium, 4922

Other groups or topics related to this group are:
ALKALI METALS
ALKALI-METAL ALLOYS
DEVARDA'S ALLOY
FERROALLOY POWDERS
FINELY DIVIDED METALS LANTHANIDE METALS
LIGHT ALLOYS
METAL DUSTS
METAL FIRES
MILD STEEL
MOLTEN METAL EXPLOSIONS
PRECIOUS METAL DERIVATIVES
PYROPHORIC METALS
REACTIVE METALS
STEEL WOOL
THORIUM FURNACE RESIDUES

Halocarbons
See entry METAL—HALOCARBON INCIDENTS

METAL SALICYLATES

Nitric acid
See Nitric acid: Metal salicylates

METAL SALTS

By far the largest class of compound in this Handbook, the metal (and ammonium) salts have been allocated into two sub-classes dependent on the presence or absence of oxygen in the anion.

The main groupings adopted for the non-oxygenated salts are:

METAL ACETYLIDES
METAL AZIDE HALIDES
METAL AZIDES
METAL AZOTETRAZOLIDES
METAL CYANIDES (AND CYANO COMPLEXES)
N-METAL DERIVATIVES
METAL HALIDES
METAL POLYHALOHALOGENATES
METAL THIOCYANATES

and for the oxosalts:

METAL ABIETATES
METAL FULMINATES
METAL NITROPHENOXIDES
METAL OXALATES
METAL OXOHALOGENATES (anion an oxo derivative of a halogen)
METAL OXOMETALLATES (anion an oxo derivative of a metal)
METAL OXONON-METALLATES (anion an oxo derivative of a non-metal)
METAL PYRUVATE NITROPHENYLHYDRAZONES
PEROXOACID SALTS (anion a peroxo derivative of a metal or non-metal)

There is a separate entry for

OXOSALTS OF NITROGENOUS BASES

In some cases it has been convenient to sub-divide the oxosalt groups into smaller sub-groups, and such sub-division is indicated under the appropriate group heading.

METAL SULFATES $M(SO_4)_n$

Aluminium

See Aluminium: Metal oxides, etc.

Magnesium

See Magnesium: Metal oxosalts
See other METAL OXONON-METALLATES

METAL SULFIDES M_mS_n

1. Byberg, K. G., *CANAMET Spec. Publ. SP87-3*, 1987, I 1.1—1.39
2. Nel, L. D., *ibid*, I 2.1—2.24
3. Hermann, F. W., *ibid*, I 3.1—3.7
4. Wheeland, K. G., *ibid*, I(B4) 5.1—5.48
5. Enright, R. J., *ibid*, II(viia) 27—44
6. Hall, A. E. (Ed.), *Sulphide Dust Explos.*; Proc. Spec. Sess. CIM Ann. Gen. Meeting, Montreal, Canadian Inst. Min. Metall., 1989
7. Liu, Q. et al., *ibid.*, 125-49
8. Rosenblum, F. et al., *CIM Bull.*, 1995, **88**(989), 44; *Chem. Abs.*, 1995, **123**, 178477g

In a special publication devoted to sulfide ore dust explosions, a dust explosion in a copper—zinc sulfide mine is discussed and related to causes and preventive measures [1]. Control measures [2] and prevention of secondary explosions are also discussed [3], and surveyed, including the need for further work [4]. The results of experimental work on the use of limestone dust to suppress explosions in pyrites dusts are presented [5]. For another special publication on ore dust explosion with numerous incidents and further studies on mechanism and control see [6]. Explosibility declines in the order pyrrotite, pyrite, chalcopyrite, sphalerite, covellite, chalcocite, galena. Pyrite at 1000 g/m^3 can give a peak pressure of 5.8 bar [7]. Self heating of broken sulfide ore, to possible ignition, has been studied. Pyrrhotite seems primarily responsible [8].

Some metal sulfides are so readily oxidised as to be pyrophoric in air. Individually indexed compounds are:

Aluminium copper(I) sulfide, 0084
* Ammonium sulfide, 4572
Antimony trisulfide, 4900
Barium sulfide, 0218
Bismuth trisulfide, 0234
* Cadmium selenide, 3953
* Caesium selenide, 4259
Calcium polysulfide, 3936
Calcium sulfide, 3935
Cerium trisulfide, 3961
Chromium(II) sulfide, 4239
Cobalt(II) sulfide, 4212
Copper iron(II) sulfide, 4263
Copper(II) sulfide, 4279
Europium(II) sulfide, 4287
Germanium(II) sulfide, 4413
Gold(III) sulfide, 0116
Iron disulfide, 4395
Iron(II) sulfide, 4394
Iron(III) sulfide, 4398
Manganese(II) sulfide, 4701
Manganese(IV) sulfide, 4702
Mercury(II) sulfide, 4602
Molybdenum(IV) sulfide, 4714
Potassium sulfide, 4665
Rhenium(VII) sulfide, 4885
Ruthenium(IV) sulfide, 4889
Samarium sulfide, 4893
Silver sulfide, 0035
Sodium disulfide, 4806
Sodium polysulfide, 4807
Sodium sulfide, 4805
Strontium sulfide, 4895

Tantalum(IV) sulfide, 4897
* Tetrakis(butylthio)uranium, 3725
* Thorium oxide sulfide, 4820
Tin(II) sulfide, 4894
Tin(IV) sulfide, 4896
Titanium(IV) sulfide, 4898
Uranium(IV) sulfide, 4899
* Zirconium oxide sulfide, 4821

See DUST EXPLOSION INCIDENTS

METAL THIOCYANATES $M(SC{\equiv}N)_n$

Oxidants

1. von Schwartz, 1918, 299—300
2. *MCA Case History No. 853*

Metal thiocyanates are oxidised explosively by chlorates or nitrates when fused, or if intimately mixed, at 400°C or on spark or flame ignition [1]. Nitric acid violently oxidised an aqueous thiocyanate solution [2].

See Nitric acid: Metal thiocyanate
Sodium nitrite: Potassium thiocyanate, 4715

METATHESIS REACTIONS

Parkin, I. *Chem. & Ind.,*., 1997, (18), 725

These are usually reactions of anhydrous transition and B metal halides with dry alkali metal salts such as the sulphides, nitrides, phosphides, arsenides etc. to give exchange of anions. They tend to be very exothermic with higher valence halides and are frequently initiated by mild warming or grinding. Metathesis is described as a controlled explosion. Mixtures considered in the specific reference above include lithium nitride with tantalum pentachloride, titanium tetrachloride and vanadium tetrachloride, also barium nitride with manganese II iodide, the last reaction photographically illustrated.

See METAL PNICTIDES

MICROWAVE OVEN HEATING

1. Gedye, R. *et al., Tetrahedron Lett.*, 1986, **27**, 279—282
2. Watkins, K. W., *J. Chem. Educ.*, 1983, **60**, 1043
3. Bedson, A., *Chem. Brit.*, 1986, **23**, 894
4. Gadge, R. *et al., Educ. Chem.*, 1988, **25**(2), 55—56
5. Gilman, L. *et al., Anal. Chem.*, 1988, **60**, 1624—1625
6. Emsley, J., *New Scientist*, 1988, Nov. 12, 56—60
7. Anon., *Lab. News* (London), 31 Oct. 1988, (409), 2
8. Anon, *Safety Digest Univ. Safety Assoc.*, 1994, (50), 3
9. *Introduction to microwave sample preparation*, Kinston, H. M., Jassie, L. B. (eds.), ACS Professional Reference Ser., Washington, American Chemical Society, 1989

10. *Microwave-Enhanced Chemistry*, Kingston H. M. & Haswall S. J. (Eds), Washington D. C., American Chemical Society, 1997
11. Anon., *Safety Digest Univ. Safety Assoc.*, 1992, **44**, 26
12. Pickford, C. J., *Chem. Brit.*, 2002, **38**(4), 22

During an investigation of microwave oven heating on the oxidation of toluene by potassium permanganate in a sealed Teflon vessel, excessively high pressures developed and a violent explosion ensued [1]. The possibility of a second hazard, that of explosion of a flammable vapour in a microwave oven, had been foreseen previously [2]. The current state of development of microwave heating to speed up sample dissolution was reviewed [3]. Use of microwave ovens for rapid preparation of derivatives in sealed Teflon vessels for analytical purposes are discussed, and the need for caution to avoid explosions due to excessive solvent volumes is stressed [4]. The desirability of heating acid digestion mixtures, or indeed any liquid, by microwave heating in a sealed container without an adequate pressure relief device is questioned [5]. General aspects of microwave heating in chemical operations have been discussed [6]. A survey showed a large number of incidents, including 13 serious cases of scalding or oven doors being blown off, caused by misuse of microwave ovens and lack of precautions, largely among biologists [7]. A microwave oven was destroyed when agar jelly was (over)heated in a flask with (probably) a too tight stopper [8]. The new text book deals with preparation of mineral, metallic, biological and chemical samples, and safety aspects and precautions for the techniques [9]. An updated and more comprehensive study of microwave techniques has been published, Chapter 16 covering safety. Most of the many incidents detailed are best described as careless handling of nitric acid in analytical digestions, and have little to do with microwaves as such. More specific points are corrosion of safety interlocks when domestic ovens are used for acid digestions, ultimately exposing operators to microwaves, and a risk of sparking, leading to ignition of any flammable vapours present, when strong solutions of sodium hydroxide are irradiated [10]. Rupture of containers fitted with bursting discs, the bursting disc remaining undamaged, suggests that containers for microwave digestion of geological samples may not always be as strong as intended [11]. It should be noted that, with the foaming to be expected of a superheated liquid, vents would easily block even should a safety valve operate. Analytical solutions prepared by microwave-assisted digestion of organics are usually grossly supersaturated with carbon dioxide, and do not always nucleate and discharge gas during transfer. Subsequent explosion of vials into which they have been transferred is reported [12].
See also SAMPLE DISSOLUTION

MILD STEEL

MCA Case History No. 947

A small mild steel cylinder suitable for high pressure at ambient temperature was two-thirds filled with liquid ammonia by connecting it to a large ammonia cylinder and cooling the smaller cylinder to —70°C by immersion in a solid carbon dioxide—acetone bath. Some hours after filling, the cylinder burst, splitting cleanly along its length. This was caused by cryogenic embrittlement and weakening of the mild steel cylinder. Special alloys are required for operations at low temperatures and high pressures.

MILK POWDER

1. Buma, T. J. *et al., Chem. Abs.*, 1977, **87**, 83300
2. Anon, *Fire Prevention*, 1990, (228), 39
3. Anon., *Loss Prev. Bull.*, 1994, (119), 5.

Lumps of powdered milk formed near the hot-air inlet of spray driers may ignite spontaneously. The thermochemical mechanism has been investigated [1]. A case of probable spontaneous combustion in milk powder which had been accidentally wetted some weeks previously is described [2]. Following two explosions in a spray drier handling dairy products, investigation showed that milk powder, in air, showed exothermicity from 195°C. The drying air had been at 210°C, it was recommended that its temperature be reduced [3]. There are also carbon monoxide dangers in using alkaline cleaners on milk drying equipment without good ventilation

See also SUGARS

See other AUTOIGNITION INCIDENTS, IGNITION SOURCES

MINIMUM IGNITION ENERGY (MIE)

1. Nuzhda, L. I. *et al., Chem. Abs.*, 1984, **101**, 156838
2. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203
3. Siwek, R. *et al., Process Safety Progr.*, 1995, **14**(2), 107
4. Carlsson, T. O. et al., *Sci Tech. Froid*, 1996, (3), 277; *Chem. Abs.*, 1997, **127**, 228940n
5. Astbury, G. R., *Org. Proc. Res. & Dev.*, 2002, **6**(6), 893

The MIE of gas—air or vapour—air mixtures can be determined from the structural formula and the molar heat of combustion of the compounds studied, and equations for the calculation are presented. The method is stated to give more accurate results than conventional methods used to assess flammability of mixtures of gas or vapour with air [1]. It is claimed that in oxygen MIEs are about a hundredfold lower than in air [2]. This has had particular implications when working with hydrogen peroxide, which decomposes to give a local oxygen atmosphere in consequent bubbles [5]. A study of the ignition behaviour of dusts, including correlation of electrical and mechanical minimum ignition spark energies and ignition temperature is made [3]. In the particular case of ammonia/air, using spark ignition, it was shown that the duration of the spark is important. Almost ten-fold variation in MIE was observed between capacitor discharge and induction coil spark generation. Less power for longer was more effective, this raises general questions about measurement and meaning of MIEs [4].

The editor has encountered numerous studies of laser ignition, usually of explosives. These demonstrate that the ignition is normally a thermal effect, caused by heating solid particles, not photochemical, and thus the MIE is not lower than other methods. This may not obtain if the light be of a frequency (visible or uv) sufficient to excite the early steps of the explosion reaction, as, for example, photodissociation of halogens to the atomic radicals which are the start of their explosive reactions with fuels.

MISTS

1. Eichorn, P., *Petroleum Refiner*, 1955, **34**(11), 194
2. Kletz, T. A., *Process Safety Progress*, 1995, **14**(4), 273
3. Hansen, O. R. et al., *Proceedings of 36th Annual Loss Prevention Symposium*, 2002, 119, Amer. Inst. Chem. Eng.

Mists are dust clouds in which the particles happen to be liquid. Should that liquid be combustible, even though it is nowhere near its flash-point, explosion is possible [1] [2]. Mist explosions attract increasing study [3]. It is possible that many vapour cloud explosions have had a mist component. The editor surmises that, under appropriate circumstances, evaporation of volatile mist by the heat of a vapour (or mist) explosion might generate a larger pressure pulse than simple thermobaric effects on air. Foams are inverse mists and should show similar explosive potential.

See DUST EXPLOSION INCIDENTS

See also VAPOUR CLOUD EXPLOSIONS

MIXING

Stuart, R. *et al., Safety Digest Univ. Safety Assoc.*, 1993, **45**, 4

The safety, and the exact products, of reactions conducted at a significant scale can depend strongly upon the order and rate of mixing reagents and solvents. In general, the potential for full heat evolution or gas elimination should not be assembled until there is sufficient heat-sink, or vent, to control these. Reference [1] records a fatality which arose after alcohol was added to sodium, rather than sodium being added to excess alcohol, when disposing of surplus metal.

See also AGITATION INCIDENTS

See also Molybdenum nitride

MOLECULAR SIEVE INCIDENTS

Examples of molecular sieve incidents other than the subentries:

Benzyl bromide, : Molecular sieve, 2731
tert-Butyl hydroperoxide, : Molecular sieves, 1692
Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide, 4073
Nitromethane, : Molecular sieve, 0455
Oxygen difluoride, : Adsorbents, 4311
1,1,1-Trichloroethane, 0737

Air

Schoofs, G. R., *AIChE J.*, 1992, **38**(9), 1385

The larger size sieves preferentially absorb nitrogen from air and may therefore generate an oxygen enriched initial stream from large air-drying beds, when brought on line after regeneration. This increases fire risks if fuels be present. This phenomenon is not shown by 3A sieves, which are therefore to be preferred.

See OXYGEN ENRICHMENT

Ethylene

Doyle, W. H., *Loss Prev.*, 1969, **3**, 15

A 5A molecular sieve, not previously soaked in dilute ethylene, was used to dry compressed ethylene gas in a flow system. An exothermic reaction attained red heat and caused explosive failure of the dryer. The smaller-pored 3A sieve is not catalytically active towards ethylene.

Triaryl phosphates

Schmitt, C. R., *J. Fire Flamm.*, 1973, (4), 113—131

A molecular sieve bed was used to purify continuously the fire-resistant hydraulic fluid (a triaryl phosphate) in a large hydraulic press. Periodically the sieve bed was regenerated by treatment with steam, and then purified air at 205°C. After 9 years of uneventful operation, the bed ignited on admission of hot air. The fuel source was traced to the accumulation of organic residues (phenols or cresols?) on the sieve which were not removed by the steam/air treatment.

MOLTEN METAL EXPLOSIONS

1. Frölich, G., *Chem. Ing. Tech.*, 1978, **50**, 861—866
2. *Molten Metals and Water Explosions*, HSE Rept., London, HMSO, 1979
3. Vaughan, G. J., *Rept. SRD R177*, Warrington, UKAEA, 1980
4. Tso, C. P., PhD Thesis, University of California, Berkeley, 1979
5. Mitin, V. P. *et al., Chem. Abs.*, 1981, **94**, 88514
6. Shoji, S. *et al., Bull. Jap. Soc. Mech. Eng.*, 1983, **26**, 791—796
7. Jacoby, J. E., *Light Met.*, 2001, 799

Factors which determine whether or not there will be a vapour explosion when a hot melt (glass or various metals) comes into contact with water have been studied experimentally. Vapour generation must be preceeded by fragmentation of the melt to give enormous heat transfer coefficients [1]. This last report [2] in a series of 6 covers general aspects and precautions relevant to foundry practice, the earlier ones each dealing with specific metals and alloys. The molten metal—water explosion phenomenon has been reviewed with 130 references. [3]. A new thermal explosion model has been proposed and used to predict reaction zones in systems containing water and molten aluminium, lead and tin, among others [4]. Aluminium alloys containing lead and bismuth prove abnormally hazardous in practice [7]. The mechanisms of explosion when molten magnesium [5] or tin [6] contact water have been studied on the small scale. Other incidents of this type are:

Aluminium, : Water (references 9,10), 0048

Copper, : Water, 4261

Tin, : Water (references 1—3), 4906

SMELT

STEAM EXPLOSIONS

See also VAPOUR EXPLOSIONS

MOLTEN SALT BATHS

1. *Guidelines for Safety in Heat Treatment, I: Use of Molten Salt Baths*, Birmingham, University of Aston, 1984
2. Baum, R., *Chem. Eng. News*, 1982, **60**(41), 29

3. Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 75
4. *Precautions in the Use of Nitrate Salt Baths*, Min. of Labour, SHW booklet, London, HMSO, 1964
5. Pieters, 1957, 30
6. *Potential Hazards in the Use of Salt Baths for Heat Treatment of Metals*, NBFU Res. Rept. No. 2., New York, 1946
7. Beck, W., *Aluminium*, 1935, **17**, 3—6
8. Clark, E. R. *et al., Chem. Abs.*, 1987, **107**, 119389

A summary of the considerable hazards which may arise from incorrect use of molten salt baths and the materials in them covers all aspects of material storage, bath use, maintenance and cleaning, disposal of used materials and firefighting [1]. An account of a disastrous laboratory explosion caused by melting together 1.3 kg of the oxidant sodium nitrite and 0.4 kg of the reducant potassium thiocyanate is remarkable in that it was claimed that the violent redox reaction on melting could not have been foreseen [2]. As well as for heat treatment, molten salt baths are also used to oxidise impurities from metal components. When filter plates excessively contaminated with polymer were lowered into the bath, an unusually fierce fire (possibly involving liberated oxygen) ensued [3].

The booklet covers hazards attendant on the use of molten nitrate salt baths for heat treatment of metals, including storage and disposal of salts, starting up, electrical heating, and emptying of salt baths. Readily oxidisable materials must be rigorously excluded from the vicinity of nitrate baths [4]. Earlier it had been reported that aluminium and its alloys if contaminated with organic matter may explode in nitrate—nitrite fused salt heating baths [5]. Uses, composition, and precautions in the use of molten salt baths are discussed. Most common causes of accidents are: steam explosions, trapping of air, explosive reactions with reducing metals (magnesium) and organic matter or cyanides from other heat treatment processes [6]. Explosions involving use of aluminium in nitrate baths have also been attributed to corrosive failure of the iron container, rather than to direct interaction with aluminium [7]. Heat treatment of aluminium—lithium and aluminium—magnesium alloys in nitrite—nitrate salt baths was studied [8].

See Sodium nitrite: Potassium thiocyanate

MOLTEN SALTS

Zhuchkov, P. A. *et al., Chem. Abs.*, 1974, **80**, 28651

The causes of furnace blasts occurring in soda-regeneration plants when water is spilt into molten sodium carbonate, sodium chloride, sodium hydroxide, sodium sulfate or sodium sulfide are discussed, together with methods of prevention.

NANOTECHNOLOGY

Sanderson K, *Chem. World*, 2005, **2**(6), 46

Nanotechnology concerns itself with the very small, but in so far as it is now a technology it mostly sells macroscopic quantities of microscopically controlled structures, and must make these by macroscopic techniques. Some proclaimed preparations

of nano-particles seem fated to remain nanotechniques by virtue of explosion hazards, even at milligram scale. The very fine products often show pyrophoricity in bulk.
See 3,6-Diazido-1,2,4,5-tetrazine
See METAL NITRATES: Organic matter
See also METATHESIS REACTIONS, ROTANES

NATURAL FIBRES

Hydrogen peroxide: Acetic acid, Jute, 4471
Nitric acid: Cellulose, 4430
Potassium chlorate: Fabric, 4011
See Calcium oxide: Water (reference 3)
COTTON
See DUST EXPLOSION INCIDENTS (reference 15)

NEUTRALISATION INCIDENTS

Incidents of several different types have arisen from reactions involving neutralisation of an acid with a base where the exotherm (57.3 kJ/equivalent for strong acid—strong base reactions) has not occurred smoothly over an extended period, but has been sudden in effect for various reasons. Individually indexed neutralisation incidents are:
† Formaldehyde, : Magnesium carbonate hydroxide, 0415
Potassium hydroxide, : Acids, 4422
Sodium carbonate, 0549
Sulfuric acid, : 4-Methylpyridine, 4473
Sulfuric acid, : Diethylamine, 4473
2,4,6-Trichloro-1,3,5-triazine, : 2-Ethoxyethanol, 1035
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

NITRAMINE—METAL COMPLEXES $O_2NN \nRightarrow M$

Palopali, S. F. *et al., Inorg. Chem.*, 1988, **27**, 2963—2971
Complexes of the explosively unstable nitramine ligands *N*-nitromethylamine (HL), N,N′-dinitrodiaminoethane (H_2L'), and 5-nitraminotetrazole (H_2L'') with ammine derivatives of divalent copper, nickel or palladium explode on heating or under a hammer blow. Compounds prepared were :

$Cu(NH_3)_2L_2$, $Cu(en)L_2$, $Cu(NH_3)_2L'$, $Ni(H_2O)_4L'$, $Ni(NH_3)_3L'$, $Pd(NH_3)_2L'$, $[Cu(en)_2]\ [[Cu(en)_2L'_2]_2\ \mu L']$.

Ligand bonding to metal was via O and/or N.

The individual ligands are :
- *N,N′*-Dinitro-1,2-diaminoethane, 0912
- 5-*N*-Nitroaminotetrazole, 0414
- *N*-Nitromethylamine, 0476

See other N—NITRO COMPOUNDS

NITRATING AGENTS

1. Dubar, J. *et al., Compt. rend. Ser. C*, 1968, **266**, 1114
2. Buckley, E. *et al., Chem. & Ind.*, 1978, 124—125
3. Feuer, H. *et al., J. Org. Chem.*, 1978, **43**, 4677

The potentially explosive character of various nitration mixtures (2-cyanopropyl nitrate in acetonitrile; solutions of dinitrogen tetraoxide in esters, ethers or hydrocarbons; dinitrogen pentaoxide in dichloromethane; nitronium tetrafluoroborate in sulfolane) are mentioned [1]. Use of mixtures of fuming nitric acid—sulfuric acid in acetic anhydride to highly nitrate naphthalene derivatives is accompanied by formation of tetranitromethane, and care is required [2]. When propyl nitrate is used as a nitrating agent, effective cooling at —60°C is necessary to deal with the highly exothermic reaction [3].

NITRATION INCIDENTS

1. Biasutti, 1974, 8, 123—125
2. Albright, Hanson, 1976
3. Obnovlenskii, P. A. *et al., Chem. Abs.*, 1975, **83**, 168135
4. Raczynski, S., *Chem. Abs.*, 1963, **59**, 15114e
5. Rüst, 1948, 317—319
6. Biasutti, 1981
7. Albright, M. F., in Kirk-Othmer, 1981, Vol. 15, 841—853
8. Evans, F. W. *et al., Loss Prev. Safety Prom. Proc. Ind.*, 191—197, Frankfort, DECHEMA, 1978
9. Zeller, J. R., Paper 28, *ACS CHAS Div. Symp. Chem. Haz. Proc. Rev.*, 1984; Ch. 11 in *Chem. Proc. Haz. Rev.*, ACS Sympo. Ser. No. 274, 107—114, Washington, ACS, 1985
10. Sokhenko, V. I. *et al., Chem. Abs.*, 1987, **107**, 9818
11. Sommer, E. *et al., Proc. 7th Sympos. Chem. Probl. Stabil. Explos.*, 1986, 175—180
12. Wiss, J. *et al., J. Loss Prevention*, 1995, **8**(4), 205
13. Wörsdörfer, U. *et al., Prax. Sicherheitstech.* 1997, **4**, 355; *Chem. Abs.*, 1998, **128**, 77116m
14. Urben, P. G., *J. Chem. Educ.*, 1992, **69**, 334
15. Editor's comments, 1993
16. Rigas, F. *et al., Ind. Eng. Chem. Res.*, 1997, **36**, 5068
17. Gustin, J-L., *Org. Process Res. & Dev.*, 1998, 2, 27

Accident statistics formerly showed nitration as the most widespread and powerfully destructive industrial unit process operation (it has been overtaken by polymerisation). This is because nitric acid can, under certain conditions, effect complete and highly exothermal conversion of organic molecules to gases, the reactions often being capable of acceleration to deflagration or detonation. Case histories are described and safety aspects of continuous nitration processes are discussed in detail [1]. Of the 25 chapters of the book [2], each a paper presented at the symposium on 'Advances in Industrial and Laboratory Nitrations' at Philadelphia in 1975, 3 deal with safety aspects of nitration: Ch. 8, Hanson, C. *et al., Side Reactions during Aromatic Nitration*; Ch. 22, Biasutti, G. S., *Safe Manufacture and Handling of Liquid Nitric Esters*; Ch. 23, Brunberg, B., *Safe Manufacture and Handling of Liquid Nitric Esters: the Injector Nitration Process.*

Reaction parameters important for control of continuous nitration systems were identified, as were secondary parameters useful for diagnostic/protective purposes. The algorithms developed were successfully applied to a pilot plant for continuous nitration of 2-pyridone in acetic anhydride [3]. Technological difficulties associated with methods of reducing explosion hazards in aromatic nitration were discussed [4], and many case histories of violent incidents during nitration operations have been collected [5,6]. In a comprehensive review, general safety precautions and information relevant to nitration are reported [7]. Safety considerations relevant to the development and design of a new industrial nitration plant are detailed [8]. An account is given of the relatively inexpensive methods used to develop safe processing and reaction conditions for the conversion of 5-chloro-1,3-dimethyl-1*H*-pyrazole to the 4-nitro derivative [9]. A detailed study of safety optimisation of aromatic nitration, with the particular example of chlorobenzene is reported in [12]. A further review of processing problems for organic nitro-compounds, essentially aromatics, with extensive references, has appeared [17].

Use of sensors to measure gas phase NO_2 concentration, electrical conductivity of the reaction mass, and gas phase temperatures at several critical points in semi-continuous nitration reactors permits safe operation of nitration processes [10]. The use of non-aqueous titration analysis in the control of nitration processes in explosives manufacture is discussed [11]. Counter-intuitively, safety of spent acids from nitrate ester production is decreased by lowered nitric acid content. This is because the runaway reaction is oxidation of alcohols, kinetically easier than that of the dissolved nitrate esters from which the alcohols are reformed by hydrolysis [16].

Nitration is also a frequent cause of laboratory accident. A mixed acid nitration of arylcarboxylic esters, the substrate dissolved in sulphuric acid and nitric added to this mix, was found to be increasingly thermally unstable with increasing nitric acid excess. Process safety could not be guaranteed with above 10% excess [13]. Some suggestions on safer, cleaner nitration procedures are given in [14]. There would be fewer laboratory nitration mishaps if reaction equations were written in full and balanced so that the usual reaction was seen as an acid catalysed dehydration of nitric acid, the supposed substrate being only a scavenger of the product of dehydration (and often also a base in the nitration environment). The competing radical oxidation reaction which is the direct cause of accident is not greatly acid catalysed, but autocatalytic and catalysed by free $\cdot NO_2$. Consideration of mechanism can usually produce safer procedures than scholastic labours in the academic literature, whereby methods are often inherited unchanged from the 19th century. It should be noted that most of the studies above come from the heavy chemical industry, who are economically constrained to use rather wet conditions (and nitration is a dehydration!) and commonly work with two phase mixtures. Their conclusions do not necessarily, or even usually, represent optimal laboratory procedure, especially for homogeneous nitrations [15].

The products of nitration are generally destabilised by traces of the acid reagents used in nitration, but also by base. They need thorough washing for safe drying in bulk.

Individually detailed nitration incidents are found under:

2-Chloro-1,3-dinitro-5-trifluoromethylbenzene, 2633
Dimethyl 4-acetamidophthalate: Nitric acid, 3514
4,6-Dinitro-1,3-benzenediol, 2191
Dinitrogen tetraoxide, : Laboratory grease, 4720
2-Methyl-4-nitroimidazole, 1471
3-Methyl-4-nitropyridine *N*-oxide, 2310
Nitric acid, 4430
3-Nitroaniline: Nitric acid, Sulfuric acid, 2307
Nitronium perchlorate, : 1,2-Epoxides, 4022
2,2′-Oxybis(ethyl nitrate), 1594
Sodium nitrate, : Phenol, Trifluoroacetic acid, 4716

See also NITRATING AGENTS, VACUUM OVENS
See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

NITRIDES

There are three anions that may loosely claim to be nitrides. Pentazolides (salts of cyclic N_5^-) will all be explosive. Some azides (salts of N_3^-) fall just short of being explosive but all are violently unstable. The true nitrides, nominal derivatives of N^{3-}, are more various. In addition to some ionic structures, there are polymeric covalent examples, and some monomeric covalent ones, while most of those of transition metals are best considered as alloys. Several are endothermic and explosive, almost all are thermodynamically very unstable in air with respect to the oxide. Many are therefore pyrophoric if finely divided and also may react violently with water and, more particularly, acids, especially oxidising acids. A few are of considerable kinetic stability in these circumstances. There is no very clear classification of probable safety by position in the periodic table but polymeric and alloy structures are in general the more stable. Individual nitrides having entries:

* Ammonium nitridoosmate, 4518
Antimony(III) nitride, 4724
Barium nitride, 0219
* Barium nitridoosmate, 0213
Bismuth nitride, 0230
Cadmium nitride, 3954
Caesium nitride, 4260
Calcium nitride, 3940
* Carbonyl(pentasulfur pentanitrido)molybdenum, 0532
Cerium nitride, 3959
* Chloro-1,2,4-triselenadiazolium chloride, 4083
Chromium nitride, 4231
Cobalt(III) nitride, 4208
Copper(I) nitride, 4283
Diseleniumdisulfur tetranitride, 4763
Disulfur dinitride, 4749
Gold(I) nitride—ammonia, 0117

Gold(III) nitride trihydrate, 0118
* Iodinated poly(sulfur nitride), 4617
Lead nitride, 4748
Lithium nitride, 4681
Magnesium nitride, 4693
Mercury nitride, 4610
Molybdenum nitride (mixture of 3), 4709
Pentasulfur hexanitride, 4778
Plutonium nitride, 4721
* Poly(disilicon nitride), 4752
* Poly(selenium nitride), 4725
Poly(sulfur nitride), 4723
Potassium nitride, 4666
* Potassium nitridoosmate, 4646
Rhenium nitride tetrafluoride, 4338
Rubidium nitride, 4722
Silver nitride, 0038
* Silver trisulfurpentanitridate, 0024
Sodium nitride, 4718
* Sodium tetrasulfur pentanitridate, 4769
* Sodium tetrasulfur pentanitridate, 4769
Sodium trisulfurtrinitridate, 4755
Tetraselenium dinitride, 4751
* Tetraselenium tetranitride, 4765
Tetrasulfur dinitride, 4750
Tetrasulfur tetranitride, 4764
* Tetratellurium tetranitride, 4767
* Tetratellurium tetranitride, 4767
Thallium(I) nitride, 4726
Trifluorosulfur nitride, 4332
Trisilver tetranitride, 0040
Tritellurium tetranitride, 4766
Trithorium tetranitride, 4768
Uranium(III) nitride, 4727
Zirconium nitride, 4728
See Pentazole
See AZIDES, METAL PNICTIDES

NITRITE SALTS OF NITROGENOUS BASES $N^+ NO_2^-$

1. Mellor, 1940, Vol. 8, 289, 470—472
2. Ray, P. C. *et al., J. Chem. Soc.*, 1911, **99**, 1470; 1912, **101**, 141, 216

Ammonium and substituted-ammonium nitrite salts exhibit a range of instability, and reaction mixtures which may be expected to yield these products should be handled with care. Ammonium nitrite will decompose explosively either as the solid, or in conc. aqueous solution when heated to 60—70°C. Presence of traces of acid lowers the decomposition temperature markedly. Hydroxylammonium nitrite appears to be so unstable that it decomposes immediately in solution. Hydrazinium(1+) nitrite is a solid which explodes violently on percussion, or less vigorously if heated rapidly, and hydrogen azide may be a product of decomposition [1]. Mono- and di-alkylammonium nitrites decompose at temperatures below 60—70°C, but usually without violence [2]. Individual entries are:

Ammonium nitrite, 4516
Hydrazinium nitrite, 4543
Methylammonium nitrite, 0502
See other OXOSALTS OF NITROGENOUS BASES

NITROACYL HALIDES — $o\text{-}O_2NArCO.Cl$, etc.

Aromatic acyl halides containing a nitro group adjacent to the halide function show a tendency towards violent thermal decomposition. The few individually indexed compounds are:

* 2,4-Dinitrobenzenesulfenyl chloride, 2092
2,4-Dinitrobenzenesulfonyl chloride, 2093
2,4-Dinitrophenylacetyl chloride, 2897
4-Hydroxy-3-nitrobenzenesulfonyl chloride, 2139
3-Methoxy-2-nitrobenzoyl chloride, 2910
4-Methoxy-3-nitrobenzoyl chloride, 2911
3-Methyl-2-nitrobenzoyl chloride, 2908
2-Nitrobenzoyl chloride, 2649
2-Nitrophenylacetyl chloride, 2909
4-Nitrothiophene-2-sulfonyl chloride, 1384
See other ACYL HALIDES

NITROALKANES — RNO_2

1. *Nitroparaffins*, TDS1, New York, Commercial Solvents Corp.,1968
2. Hass, H. B. *et al., Chem. Rev.*, 1943, **32**, 388
3. Noble, P. *et al., Chem. Rev.*, 1964, **64**, 20
4. Murray, S. B. *et al., Can. Pat. Appl.* 2123170, 1995

Nitromethane is a detonable explosive, nitroethane can be detonated if both hot and under strong confinement, other nitroalkanes are mild oxidants under ordinary conditions, but precautions should be taken when they are subjected to high temperatures and pressures, since violent reactions may occur [1]. Explosives are described consisting of nitromethane stabilised for transport by admixture with nitroethane or nitropropane, then resensitised by addition of an amine [4]. The polynitroalkanes, being more in oxygen balance than the mono-derivatives, tend to explode more easily [2], and caution is urged, particularly during distillation [3].

Individually indexed compounds are:

* Aluminium chloride—nitromethane, 0063
* Chloronitromethane, 0395
* Ethyl 2-nitroethyl ether, 1657

- * Nitroacetone, 1180
  - *tert*-Nitrobutane, 1655
  - Nitroethane, 0865
  - Nitromethane, 0455
- * Nitrooximinomethane, 0408
  - 2-Nitropropane, 1260
  - 1-Nitropropane, 1259
- * Potassium 1-nitroethane-1-oximate, 0753
- * Tribromonitromethane, 0313
- * Trichloronitromethane, 0330
- * Tris(hydroxymethyl)nitromethane, 1658

See also POLYNITROALKYL COMPOUNDS

Alkali metals, or Inorganic bases

Watts, C. E., *Chem. Eng. News*, 1952, **30**, 2344

Contact of nitroalkanes with inorganic bases must be effected under conditions which will avoid isolation in the dry state of the explosive metal salts of the isomeric *aci*-nitroparaffins.

Hopcalite

See HOPCALITE

Metal oxides

1. Hermoni, A. *et al., Chem. & Ind.*, 1960, 1265
2. Hermoni, A. *et al., Proc. 8th Combust. Symp.*, 1960, 1084—1088

Contact with metal oxides increases the sensitivity of nitromethane, nitroethane and 1-nitropropane to heat (and of nitromethane to detonation). Twenty-four oxides were examined in a simple quantitative test, and a mechanism was proposed. Cobalt, nickel, chromium, lead and silver oxides were the most effective in lowering ignition temperatures [1]. At 39 bar initial pressure, the catalytic decomposition by chromium or iron oxides becomes explosive at above 245°C [2].

Sodium or Potassium bicarbonate

Kirk-Othmer, 1996, Vol. 17, 216

Dry powder fire extinguishers containing bicarbonate should not be used on nitromethane or nitroethane.

See aci-NITRO SALTS, C—NITRO COMPOUNDS

NITROALKENES $C{=}CNO_2$

Several nitroalkenes show high reactivity and/or low stability, individually indexed compounds being:

- * 3,3-Dimethyl-1-nitro-1-butyne, 2389
  - 2,3-Dinitro-2-butene, 1506
  - 1,1-Dinitro-3-butene, 1505
  - 4-Fluoro-4,4-dinitrobutene, 1454
- * 3-Methyl-4-nitro-1-buten-3-yl acetate, 2831

* 3-Methyl-4-nitro-2-buten-1-yl acetate, 2832
4-Nitro-1-butene, 1567
2-Nitropropene, 1179
Tetranitroethylene, 1006

NITROALKYL PEROXONITRATES $O_2NC—COONO_2$

See Dinitrogen tetraoxide: Cycloalkenes, etc.

NITROANILINES O_2NArNH_2

Chlorine (or other oxidant),

Hydrochloric acid
See Hydrogen chloride: Chlorine, Dinitroanilines

NITROAROMATIC—ALKALI HAZARDS

1. Merz, V. *et al., Ber.*, 1871, **4**, 981—982
2. Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389—390
3. (*MCA Data Sheets*); *Haz. Chem. Data*, 1975; *491M*, 1975
4. Bretherick, L., *Proc. 6th Int. Symp. Prev. Occ. Risks Chem. Ind.*, 539—546, Heidelberg, ISSA, 1979 (and additional bibliography)
5. Howes, R. J., private comm., 1979
6. Capellos, C. *et al., Chem. Abs.*, 1982, **96**, 88003

It is widely stated in the usual reference texts that nitroaromatic compounds and more particularly polynitroaromatic compounds may present a severe explosion risk if subjected to shock, or if heated rapidly and uncontrollably, as in fire situations. However, the same reference texts make no mention of the fact that there is also a risk of violent decomposition or explosion when nitroaromatic compounds are heated more moderately with caustic alkalies, even when water or organic solvents are also present. It was known more than 100 years ago that mononitroaromatics (nitro-benzene, -toluene, -naphthalene) would react violently on heating with caustic alkalies ‘with generation of 1½ foot flames’, and that dinitro compounds were almost completely carbonised [1]. By 1914 the potential hazards involved in heating di-or tri-nitroaryl compounds with alkalies or ammonia were sufficiently well recognised for a general warning on the possibilities of violent or explosive reactions in such systems to have been published [2]. Knowledge of these potential hazards apparently had faded to the point where they were not mentioned in standard sources of information [3].

Several industrial explosions have occurred during the past 40 years which appear to be attributable to this cause, but here has been little recognition of this or of the common features in many of the incidents. Too little investigational work in this area has been published to allow any valid conclusions to be drawn as to the detailed course of the observed reactions. However, it may be more than coincidence that in all the incidents reported, the structures of the nitroaromatic compounds involved were such that *o*- or *p*-*aci*-nitroquinonoid salt species could have been formed under the reaction conditions. Many of these salts are of very limited thermal stability. All of the available (circumstantial) evidence was collected and published [4]. Limited work by

DTA showed that *o*-nitrophenol and sodium hydroxide gave a sharp exotherm at 46°, and *p*-nitrophenol at 95°, while *m*-nitrophenol gave no significant evidence of reaction below 200°C. *o*-Nitroaniline gave a sharp exotherm at 217°, and *p*-nitroaniline at 246°C [5]. Electronic excitation of TNT leads to formation of *aci*-quinonoid transient intermediates, and action of various bases leads to deflagration of molten TNT [6].

Individually indexed incidents of this type are:
2-Chloro-4-nitrotoluene, : Sodium hydroxide, 2708
2,4-Dinitrotoluene, 2722
2,4-Dinitrotoluene, : Sodium oxide, 2722
Lithium 4-nitrothiophenoxide, 2170
4-Methyl-2-nitrophenol, 2763
2-Nitroanisole, : Sodium hydroxide, Zinc, 2764
Nitrobenzene, : Alkali, 2255
Sodium 2,4-dinitrophenoxide, 2108
Sodium 2-nitrothiophenoxide, 2175
Sodium 4-nitrophenoxide, 2176
2,4,5-Trinitrotoluene, 2698
See also aci-NITROQUINONOID COMPOUNDS, C—NITRO COMPOUNDS

NITROARYL COMPOUNDS $ArNO_2$

1. Chervin, S. *et al., Proc. Workshop Microcalorim. Energ. Mater.*, 1997, R1; *Chem. Abs.*, 1998, **129**, 262429z

This group covers aromatic nuclei bearing one nitro group; most mono-nitro benzenes can be persuaded to detonate by a tetryl booster; few are an immediate danger in the absence of other sources of energy. Calorimetric studies [1] suggest that nitroaryl compounds decompose by an autocatalytic mechanism, and thus stability may depend upon thermal history. Individually indexed compounds are:
4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3260
2-Amino-5-nitrophenol, 2309
2-(2-Aminoethylamino)-5-methoxynitrobenzene, 3166
* Amminebarium bis(nitrophenylide), 3512
1,3-Bis(trifluoromethyl)-5-nitrobenzene, 2880
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2641
N-Bromo-3-nitrophthalimide, 2879
tert-Butyl 4-nitroperoxybenzoate, 3394
6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2095
4-Chloro-2,5-diethoxynitrobenzene, 3295
5-Chloro-2-nitrobenzaldehyde, 2648
5-Chloro-2-nitrobenzyl alcohol, 2714
4-Chloro-2-nitrobenzyl alcohol, 2712
6-Chloro-2-nitrobenzyl bromide, 2667
4-Chloro-2-nitrobenzyl chloride, 2675
4-Chloro-3-nitrobenzaldehyde, 2647
4-Chloro-3-nitrobenzyl alcohol, 2713
4-Chloro-3-nitrotoluene, 2709
1-Chloro-4-(2-nitrophenyl)-2-butene, 3264

N-Chloro-4-nitroaniline, 2224
2-Chloro-4-nitrobenzyl chloride, 2674
2-Chloro-4-nitrotoluene, 2708
2-Chloro-5-nitrobenzaldehyde, 2645
2-Chloro-5-nitrobenzenesulfonic acid, 2137
2-Chloro-5-nitrobenzyl alcohol, 2711
2-Chloro-6-nitrobenzaldehyde, 2646
4-Chloronitrobenzene, 2135
2-Chloronitrobenzene, 2134
4-Cyano-3-nitrotoluene, 2912
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2664
2,6-Di-*tert*-butyl-4-nitrophenol, 3659
Dichloronitrobenzene, 2096
Diethyl 4-nitrophenyl phosphate, 3323
Diethyl 4-nitrophenyl thionophosphate, 3322
2,4-Difluoronitrobenzene, 2102
Dimethyl 4-acetamino-5-nitrophthalate, 3509
Disodium 4-nitrophenylphosphate, 2178
5-Fluoro-2-nitrophenol, 2160
5-Hydroxy-2-nitrobenzaldehyde, 2688
4-Hydroxy-3-nitrobenzaldehyde, 2687
3-Hydroxy-4-nitrobenzaldehyde, 2686
Lanthanum 2-nitrobenzoate, 3809
3-Methoxy-2-nitrobenzaldehyde, 2932
3-Methoxy-2-nitrobenzoyldiazomethane, 3118
2-Methoxy-5-nitroaniline, 2798
3′-Methyl-2-nitrobenzanilide, 3638
4-Methyl-3-nitrobenzenesulfonic acid, 2769
* 2-Methyl-4-nitroimidazole, 1471
3-Methyl-4-nitrophenol, 2762
2-Methyl-5-nitroaniline, 2797
2-Methyl-5-nitrobenzenesulfonic acid, 2768
2-Methyl-5-nitrobenzimidazole, 2935
* *N*-Methyl-*p*-nitroanilinium 2(*N*-methyl-*N*-*p*-nitrophenylaminosulfonyl)ethylsulfate, 3707
Nickel 2-nitrophenoxide, 3458
4-Nitroacetanilide, 2945
2-Nitroacetophenone, 2930
2-Nitroaniline, 2306
3-Nitroaniline, 2307
4-Nitroaniline, 2308
4-Nitroaniline-2-sulfonic acid, 2312
4-Nitroanilinium perchlorate, 2343
2-Nitroanisole, 2764
2-Nitrobenzaldehyde, 2682
3-Nitrobenzaldehyde, 2683

4-Nitrobenzaldehyde, 2684
Nitrobenzene, 2255
3-Nitrobenzenesulfonic acid, 2261
4-Nitrobenzoic acid, 2691
2-Nitrobenzoic acid, 2689
3-Nitrobenzoic acid, 2690
2-Nitrobenzonitrile, 2658
3-Nitrobenzoyl nitrate, 2660
2-Nitrobenzyl alcohol, 2765
3-Nitrobenzyl alcohol, 2766
4-Nitrobenzyl alcohol, 2767
2-Nitrobenzyl bromide, 2706
2-Nitrobenzyl chloride, 2710
4-Nitrobenzyl chloride, 2710
4-Nitrodiphenyl ether, 3465
mixo-Nitroindane, 3134
4-Nitroisopropylbenzene, 3151
Nitromesitylene, 3152
1-Nitronaphthalene, 3243
3-Nitroperchlorylbenzene, 2136
2-Nitrophenol, 2258
3-Nitrophenol, 2259
4-Nitrophenol, 2260
N-(2-Nitrophenyl)-1,2-diaminoethane, 2996
3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid, 3125
1-(2-Nitrophenyl)-5-phenyltetrazole, 3596
4-Nitrophenylacetic acid, 2933
3-Nitrophenylacetylene, 2900
4-Nitrophenylphosphorodichloridate, 2151
4-Nitrophenylpropan-2-one, 3136
2-Nitrophenylpropiolic acid, 3107
2-Nitrophenylsulfonyldiazomethane, 2696
3-Nitrophthalic acid, 2901
3-Nitropropiophenone, 3135
5-Nitrosalicylhydrazide, 2774
Nitroterephthalic acid, 2902
4-Nitrotoluene, 2760
mixo-Nitrotoluene, 2758
Potassium 4-nitrophenoxide, 2167
Scandium 3-nitrobenzoate, 3810
Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3499
Sodium 3-nitrobenzenesulfonate, 2177
5,10,15,20-Tetrakis(2-nitrophenyl)porphine, 3901
Thallium(I) 2- or 4-nitrophenoxide, 2179
Yttrium 4-nitrobenzoate trihydrate, 3811
See also NITROALKANES, POLYNITROARYL COMPOUNDS

NITROARYLPHOSPHINIC ACIDS **$O_2NArP(O)HOH$**

Rowbotham, P. M. *et al.*, UK Pat. 2 048 883, 1980

These may be explosive under some conditions.

See other NITROARYL COMPOUNDS

NITROBENZALDEHYDES **$O_2NC_6H_3(X)CO.H$**

Cardillo, P. *et al., Proc. 5th Int. Sympos. Loss Prev. Saf. Prom. Process Ind.*, Cannes, Paper P16, 1—14, SCI (Paris), 1986

A series of 11 nitrobenzaldehydes was examined by TGA, DSC and ARC techniques. Only 5-hydroxy-2-nitrobenzaldehyde decomposed exothermally in an unsealed container, but all did so in sealed capsules, under dynamic, isothermal or adiabatic conditions, with evolution of much gas. Initial decomposition temperatures in °C (compound, ARC value, and DSC value at 10°/min, respectively, followed by ARC energy of decomposition in kJ/g) were:- 2-nitro-, 176, 220, 1.44; 3-nitro-, 166, 218, 1.94; 4-nitro-, 226, 260, 1.27; 2-chloro-5-nitro-, 156, 226, .697; 2-chloro-6-nitro-, 146, 220, .832; 4-chloro-3-nitro-, 116, 165, 1.42; 5-chloro-2-nitro-, -, 240, -; 3-hydroxy-4-nitro-, -, 200, -; 4-hydroxy-3-nitro-, -, 200, -; 5-hydroxy-2-nitro-, -, 175, -; 3-methoxy-4-nitrobenzaldehyde, -, 245°C, -. 4-Nitrobenzaldehyde showed by far the highest self-heating rate in ARC tests (approaching 100°/min at 240°C) anf the final pressure exceeded 170 bar when the pressure relief operated. The results are compared with those from various nitrobenzyl derivatives.

Individually indexed compounds are:
5-Chloro-2-nitrobenzaldehyde, 2648
4-Chloro-3-nitrobenzaldehyde, 2647
2-Chloro-5-nitrobenzaldehyde, 2645
2-Chloro-6-nitrobenzaldehyde, 2646
5-Hydroxy-2-nitrobenzaldehyde, 2688
4-Hydroxy-3-nitrobenzaldehyde, 2687
3-Hydroxy-4-nitrobenzaldehyde, 2686
3-Methoxy-2-nitrobenzaldehyde, 2932
4-Nitrobenzaldehyde, 2684
3-Nitrobenzaldehyde, 2683
2-Nitrobenzaldehyde, 2682
See NITROBENZYL COMPOUNDS (next below)

NITROBENZYL COMPOUNDS **$O_2NC_6H_4CH_2X$**

1. Cardillo, P. *et al., J. Chem. Eng. Data*, 1984, **29**, 348—351
2. Cardillo, P. *et al., Proc. 5th Nat. Congr. Calorim. Therm. Anal.*, Trieste, 1983
3. Cardillo, P. *et al., Proc. 15th Nat. Congr. Ital. Chem. Soc.*, 349—350, 1984; *Chim. e Ind.* (Milan), 1986, **68**(6), 68—70
4. Cardillo, P. *et al., Chim. e Ind.* (Milan), 1985, **67**, 403—405

Thermal stabilities of the six *o*-, *m*- and *p*-nitrobenzyl bromides and chlorides were studied comparatively by TGA, DSC and ARC techniques. In open sample containers, only *o*-nitrobenzyl bromide decomposed exothermally, but in sealed capsules all the compounds decomposed exothermally after melting, with abundant gas evolution.

The bromides were less stable than the chlorides, and *o*- isomers less stable than others. Very high self-heating rates (> 10°C/min), pressure increase rates (20 bar/min) and final pressures (> 170 bar, when relief valve opened) were observed for all samples in the ARC runs [1]. The effect of halogen substitution in the ring upon thermal stability of nitrobenzyl halides was studied by DTA, DSC and ARC techniques. The latter gave the following results for sealed bombs (onset of exotherm °C, maximum temperature °C and calculated energy of decomposition in kJ/g, respectively). 6-Chloro-2-nitrobenzyl bromide, 165, 306, 0.85; 4-chloro-2-nitrobenzyl chloride, 151, 230, 1.01. The bromide was the least stable, and above 190°C the self-heating rate (> 10°/min) prevented adiabatic operation of the calorimeter, and the pressure very rapidly approached 130 bar [2]. ARC examination of some industrially important potentially thermally unstable nitrobenzyl alcohols gave the following results (onset of exothermic decomposition °C, final temperature °C and calculated energy of decomposition in kJ/g, repectively). 2-Nitrobenzyl alcohol, 201, 343, 1.78; 3-nitro, 221, 332, 1.32; 4-nitro, 236, 310, 0.93; 5-chloro-2-nitro, 191, 286, 1.15; 4-chloro-3-nitro, 211, 315, 1.15; 4-chloro-2-nitro, 201, 229, 1.19; 2-chloro-5-nitro, 211, 329, 1.38 [3]. ARC results for 2-chloro-4-nitrobenzyl chloride are 216, 261, 1.01 [4].

Individually indexed compounds are:
5-Chloro-2-nitrobenzyl alcohol, 2714
4-Chloro-2-nitrobenzyl alcohol, 2712
6-Chloro-2-nitrobenzyl bromide, 2667
4-Chloro-2-nitrobenzyl chloride, 2675
4-Chloro-3-nitrobenzyl alcohol, 2713
2-Chloro-4-nitrobenzyl chloride, 2674
2-Chloro-5-nitrobenzyl alcohol, 2711
2,6-Dinitrobenzyl bromide, 2668
4-Nitrobenzyl alcohol, 2767
3-Nitrobenzyl alcohol, 2766
2-Nitrobenzyl alcohol, 2765
2-Nitrobenzyl bromide, 2706
4-Nitrobenzyl chloride, 2710
2-Nitrobenzyl chloride, 2710
See other BENZYL COMPOUNDS

NITRO COMPOUNDS $C—NO_2$, $N—NO_2$

The presence of one or more nitro groups (with 69.6% oxygen) linked to C or N in an organic compound may have a significant effect on the reactivity, oxygen balance and stability of the compound. (Compounds with a nitro group linked to O, nitrate esters, are of very much lower stability and are dealt with separately). The class has been subdivided into the separately treated groups:

Other relevant entries are:
aci-NITRO SALTS
aci-NITROQUINONOID COMPOUNDS
METAL NITROPHENOXIDES

N—NITRO COMPOUNDS
C-NITRO COMPOUNDS
NITROACYL HALIDES
NITROALKANES
NITROALKENES
NITROALKYL PEROXONITRATES
NITROAROMATIC—ALKALI HAZARDS
NITROARYL COMPOUNDS
NITROARYLPHOSPHINIC ACIDS
NITROBENZYL COMPOUNDS
POLYNITROALKYL COMPOUNDS
POLYNITROARYL COMPOUNDS
POLYNITROAZOPYRIDINES

C—NITRO COMPOUNDS $C—NO_2$

1. Engelke, R. *et al., Int. J. Chem. Kinetics*, 1986, **18**, 1205
2. Constantinou, C. P., *Phil. Trans. R. Soc. London Ser. A*, 1992, **339**, 403

In general, *C*-nitro compounds are more stable than *N*-nitro compounds because of the higher bonding energies in the former type. Evidence is offered [1] that decomposition and explosion of many nitro-derivatives proceeds through the aci-form, and that sensitivity corresponds to the proportion of that present. In terms of this work, sensitisation by very small proportions of soluble organic bases is most important; this is not limited to nitroalkanes. TNT can apparently be brought to the sensitivity of lead azide by this means. For a physicist's view of this sensitisation, see [2]. All but one of the separately treated groups named in the previous entry deal with *C*-nitro compounds, and some individually indexed compounds are:

2-Amino-4,6-dihydroxy-5-nitropyrimidine, 1432
2-Carbamoyl-2-nitroacetonitrile, 1113
5-Chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole, 1858
Mercury(II) 5-nitrotetrazolide, 0977
1-Methylamino-1-methylthio-2-nitroethene, 1591
Methylnitrothiophene, 1844
3-Nitro-1,2,4-triazolone, 0712
Nitroacetaldehyde, 0759
2-Nitroethanol, 0867
2-Nitroethanonitrile, 0707
Nitromethane, 0455
5-Nitrotetrazole, 0386
Potassium 1-nitroethoxide, 0802
Potassium 2,5-dinitrocyclopentanonide, 1841
Sodium 5-nitrotetrazolide, 0544
* Sodium diformylnitromethanide hydrate, 1073

N—NITRO COMPOUNDS $N—NO_2$

van Romburgh, P., *Chem. Weekblad*, 1934, **31**, 732—733

Many *N*-nitro compounds show explosive instability, arising from the low N—N bonding energy, and the explosive properties of *N*-alkyl-*N*-nitroarylamines have been discussed. Individually indexed compounds are:

1-Amino-3-nitroguanidine, 0493
Ammonium 1,2-ethylenebis(nitramide), 0968
3,3′-Azo-(1-nitro-1,2,4-triazole), 1397
Azo-*N*-nitroformamidine, 0821
Bis(2-azidoethoxymethyl)nitramine, 2475
* Bis(2-nitratoethyl)nitric amide, 1597
1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0799
N-Butyl-*N*-2-azidoethylnitramine, 2523
N,N′-Diacetyl-*N,N′*-dinitro-1,2-diaminoethane, 2420
1,3-Diazido-2-nitroazapropane, 0820
1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane, 3044
N,N′-Dimethyl-*N,N′*-dinitrooxamide, 1510
Dinitramine, 4436
N,N′-Dinitro-1,2-diaminoethane, 0912
1,3-Dinitro-2-imidazolidinone, 1139
N,N′-Dinitro-*N*-methyl-1,2-diaminoethane, 1272
N-Fluoro-*N*-nitrobutylamine, 1640
2-Hydroxy-4,6-bis(nitroamino)-1,3,5-triazine, 1119
Lead methylenebis(nitramide), 0411
1-Methyl-3-nitro-1-nitrosoguanidine, 0872
1-Methyl-3-nitroguanidinium nitrate, 0943
1-Methyl-3-nitroguanidinium perchlorate, 0935
Methylenebis(3-nitramino-4-methylfurazan), 2819
Methylenebis(nitramine), 0481
Nitric amide, 1597
1-Nitro-3-(2,4-dinitrophenyl)urea, 2701
2-(*N*-Nitroamino)pyridine *N*-oxide, 1845
4-(*N*-Nitroamino)pyridine *N*-oxide, 1846
5-*N*-Nitroaminotetrazole, 0414
Nitroguanidine, 0480
N-Nitromethanimine, 0407
N-Nitromethylamine, 0476
Nitrourea, 0459
Silver *N*-nitrosulfuric diamidate, 0016
trans-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecahydronaphthalene, 2421
N,2,3,5-Tetranitroaniline, 2114
N,2,4,6-Tetranitroaniline, 2116
N,2,4,6-Tetranitro-*N*-methylaniline, 2702
1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine, 1600
1,3,5-Trinitrohexahydro-1,3,5-triazine, 1215
See also N-AZOLIUM NITROIMIDATES

aci-NITROQUINONOID COMPOUNDS

1. L. Bretherick's summary
2. Glowiak, B. *Chem. Abs.*, 1962, **57**, 17795

Generally, aromatic nitro compounds cannot form *aci*-nitro salts with bases unless there is an *o*- or *p*- substituent present (or is introduced by the action of the base) bearing a labile hydrogen atom. Then, isomerisation to produce *o*- or *p*-quinonoid *aci*-nitro species, then the salt, may be possible. Many salts of this type are unstable or explosive, and such species may have been involved in various incidents with nitro-aromatics and bases. It is believed that the decompositon reaction of nitro-aromatics may proceed via quinonoid isomers (in which the phenolic O shown here can be replaced by N or C, and one of the nitro-oxygens should be seen as protonated): materials which can form such isomers will usually be less stable than isomers which cannot. Although more stable to acids than alkalis, nitroaromatic compounds, especially heterocyclic ones, are sometimes found to undergo vigorous decomposition on drying, which can be acid catalysed. Good washing is advisable before insertion in drying ovens [1]. A study of the explosive properties of a variety of nitro-phenols, and lead salts thereof, has been made. It includes heats of combustion and formation, impact sensitivity and 1 sec induction explosion temperatures [2]. Individually indexed *aci*-nitro salts are:

* 1-Fluoro-2,4-dinitrobenzene, 2101
Lithium 4-nitrothiophenoxide, 2170
Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide, 2718
Potassium 4-nitrophenoxide, 2167
Potassium 6-*aci*-nitro-2,4-dinitro-1-phenylimino-2,4-cyclohexadienide, 3445
Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide, 2106
* Silver 4-nitrophenoxide, 2119
Sodium 1,4-bis(*aci*-nitro)-2,5-cyclohexadienide, 2181
Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide, 2164
Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2104
Sodium 2-nitrothiophenoxide, 2175
Sodium 3,5-bis(*aci*-nitro)cyclohexene-4,6-diiminide, 2196
Sodium 3-hydroxymercurio-2,6-dinitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2076
Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide, 2946
Sodium 4-nitrophenoxide, 2176
Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide, 2193
2,4,6-Trinitrotoluene, : Potassium hydroxide, 2697
See NITROAROMATIC—ALKALI HAZARDS

aci-NITRO SALTS —C=N(O)OM

Many *aci*-nitro salts derived from action of bases on nitroalkanes are explosive in the dry state. Individually indexed compounds are:

Ammonium *aci*-nitromethanide, 0501
Dipotassium *aci*-nitroacetate, 0668
Mercury(II) *aci*-dinitromethanide, 0703
Nitromethane, : Lithium tetrahydroaluminate, 0455

* Potassium phenyldinitromethanide, 2678
Sodium 1,3-dihydroxy-1,3-bis(*aci*-nitromethyl)-2,2,4,4-tetramethylcyclo-butandiide, 3338
* Sodium diformylnitromethanide hydrate, 1073
Thallium *aci*-phenylnitromethanide, 2719
aci-NITROQUINONOID COMPOUNDS (next above)
See NITROALKANES: Alkali metals, or Inorganic bases

NITROSATED NYLON $[-(CH_2)_mCO.N(N:O)(CH_2)_n-]_n$

Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 20
Nylon, nitrosated with dinitrogen trioxide according to Belg. Pat. 606 944 and stored cold, exploded on being allowed to warm to ambient temperature. The *N*-nitroso nylon would be similar in structure to *N*-nitroso-*N*-alkylamides, some of which are thermally unstable. Nylon components should therefore be excluded from contact with nitrosating agents.
See other NITROSO COMPOUNDS

NITROSO ARENES ArN:O

Koikov, L. N. *et al., J. Org. Chem. USSR*, 1985, **21**, 1564—1574
The general reaction of nitroso arenes with α-dimethylaminostyrenes in benzene or ether to produce $ArCO.C(NMe_2)=NC_6H_4R$ is vigorously exothermic, and with large quantities the reaction mixture may be ejected from the reaction vessel.
See NITROSO COMPOUNDS (next below)

NITROSO COMPOUNDS C—N:O, N—N:O

A number of compounds containing nitroso or coordinated nitrosyl groups exhibit instability under appropriate conditions. Individually indexed compounds are:
Ammonium *N*-nitrosophenylaminooxide, 2393
2-Chloro-1-nitroso-2-phenylpropane, 3141
1-Chloro-1-nitrosocyclohexane, 2413
N-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide, 1128
μ-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino)titanium, 3023
N,N-Dimethyl-4-nitrosoaniline, 2975
N,N′-Dimethyl-*N,N′*-dinitrosooxamide, 1509
N,N′-Dimethyl-*N,N′*-dinitrosoterephthalamide, 3278
1,2-Dimethylnitrosohydrazine, 0942
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1948
Dinitrosylnickel, 4736
Ethyl *N*-methyl-*N*-nitrosocarbamate, 1592
Lead(II) trinitrosobenzene-1,3,5-trioxide, 3588
1-Methyl-3-nitro-1-nitrosoguanidine, 0872
N-Methyl-*N*-nitrosourea, 0871
Nitritonitrosylnickel, 4737
1-Nitroso-2-naphthol, 3244
N-Nitroso-6-hexanelactam, 2418

N-Nitrosoacetanilide, 2944
Nitrosobenzene, 2254
N-Nitrosodiphenylamine, 3480
N-Nitrosoethyl-2-hydroxyethylamine, 1685
Nitrosoguanidine, 0479
2-Nitrosophenol, 2256
4-Nitrosophenol (1,4-Benzoquinone monoxime), 2257
Nitrosyl chloride, 4017
Nitrosyl cyanide, 0538
Nitrosyl tetrafluorochlorate, 3979
Nitrosylruthenium trichloride, 4138
Nitrosylsulfuric acid, 4432
Perfluoro-*tert*-nitrosobutane, 1366
* Potassium nitrosodisulfate, 4656
Sodium 4-nitrosophenoxide, 2174
1,3,5-Trinitrosohexahydro-1,3,5-triazine, 1213
Trinitrosophloroglucinol, 2110
See also NITROSATED NYLON, NITROSO ARENES, 3-NITROSOTRIAZENES

3-NITROSOTRIAZENES N=N—N(N:O)

Müller, E. *et al., Chem. Ber.*, 1962, **95**, 1255

A very unstable series of compounds, many decomposing at well below 0°C. The products formed from *N*-sodio triazenes and nitrosyl chloride explode violently on being disturbed with a wooden spatula, and are much more sensitive than those derived from silver triazenes. These exploded under a hammer-blow, or on friction from a metal spatula.

See other TRIAZENES

N—O COMPOUNDS N—O

There are a number of compounds containing N—O single bonds which are of limited or low stability. As well as the groups below there are the individually indexed compounds:

4-Amino-3-isoxazolidinone, 1134
5-Amino-3-methylisoxazole, 1498
5-Amino-3-methylthio-1,2,4-oxadiazole, 1188
2-Amino-4-methyloxazole, 1496
3-Amino-5-methylisoxazole, 1497
3-Aminoisoxazole, 1133
5-Aminoisoxazole-3-carbonamide, 1472
Ammonium *N*-nitrosophenylaminooxide, 2393
2-Aza-1,3-dioxolanium perchlorate, 0894
Azoformaldoxime, 0811
Bis(1-benzo[*d*]triazolyl) carbonate, 3592
Bis(1-benzo[*d*]triazolyl) oxalate, 3622
Bis(trifluoromethyl) nitroxide, 0634

2-*tert*-Butyl-3-phenyloxaziridine, 3400
Calcium bis(*O*-hydroxylamide), 3924
Calcium hydroxide *O*-hydroxylamide, 3923
2-Chloro-5-methylphenylhydroxylamine, 2792
N-(Chlorocarbonyloxy)trimethylurea, 1918
2-Cyano-2-propyl nitrate, 1502
μ-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino)titanium, 3023
3,4-Dichlorophenylhydroxylamine, 2236
Dicyanofurazan, 1797
3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one, 3303
3,5-Dimethylisoxazole, 1882
Dimethylthallium *N*-methylacetohydroxamate, 2002
O-(2,4-Dinitrophenyl)hydroxylamine, 2272
Disodium *N,N′*-dimethoxysulfonyldiamide, 0907
* 3-Ethyl-4-hydroxy-1,2,5-oxadiazole, 1500
2-Heptafluoropropyl-1,3,4-dioxazolone, 1806
1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0813
4-Hydroxy-3,5-dimethyl-1,2,4-triazole, 1570
1-Hydroxybenzotriazole, 2265
N-Hydroxydithiocarbamic acid, 0453
O-(2-Hydroxyethyl)hydroxylamine, 0940
1-Hydroxyimidazole *N*-oxide, 1131
1-Hydroxyimidazole-2-carboxaldoxime 3-oxide, 1473
Hydroxylamine, 4493
N-Hydroxysuccinimide, 1465
Hydroxyurea, 0475
Hyponitrous acid, 4464
4-Iodo-3,5-dimethylisoxazole, 1862
† Isoxazole, 1107
Lead hyponitrite, 4740
Lithium sodium nitroxylate, 4678
Mercury(II) formohydroxamate, 0800
* *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate, 3328
Methyl 4-bromobenzenediazoate, 2733
† Methyl nitrite, 0454
† 2-Methyl-2-oxazoline, 1564
5-Methylisoxazole, 1464
* *N*-(Methylphenylphosphinoyl)hydroxylamine, 2819
2-(4-Nitrophenoxyazo)benzoic acid, 3595
† Oxazole, 1108
2,2′-Oxybis(iminomethylfuran) mono-*N*-oxide, 3254
3-Phenyl-5-isoxazolone, 3116
N-Phenylhydroxylamine, 2349
Phenylhydroxylaminium chloride, 2359
Potassium 1-phenylethanediazoate, 2959
* Potassium cyclohexanehexone 1,3,5-trioximate, 2621

Potassium hydroxylamine-*O*-sulfonate, 4452
* Potassium methanediazoate, 0448
Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, 4657
Potassium *O*-propionohydroxamate, 1206
* Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1405
Silver benzo-1,2,3-triazole-1-oxide, 2120
* Sodium 3-methylisoxazolin-4,5-dione-4-oximate, 1415
Sodium 3-phenylisoxazolin-4,5-dione-4-oximate, 3108
* Sodium 4-chloroacetophenone oximate, 2922
Sodium nitroxylate, 4717
* Sodium tris(*O,O′*-1-oximatonaphthalene-1,2-dione)ferrate, 3865
Thallium(I) methanediazoate, 0457
N-Trifluoroacetoxy-2,4-dinitroaniline, 2887
N-Trimethylsilyl-*N*-trimethylsilyloxyacetoacetamide, 3369
1,3,4-DIOXAZOLONES
FURAZAN N-OXIDES
HYDROXYLAMINIUM SALTS
ISOXAZOLES
2H-1,2,4-OXADIAZOLO[2,3-A]PYRIDINE-2-THIONES
OXIME CARBAMATES
OXIMES
See also N-OXIDES

NON-METAL AZIDES $E(N_3)_n$

This group contains compounds with azide groups linked to non-oxygenated non-metals, individually indexed compounds being:

* Aluminium tetraazidoborate, 0059
Ammonium azide, 4521
Azidodimethylborane, 0884
Azidoiodoiodonium hexafluoroantimonate, 4355
Azidosilane, 4496
Bis(trifluoromethyl) phosphorus(III) azide, 0635
* Boron azide dichloride, 0126
* Boron azide diiodide, 0148
Boron triazide, 0153
Diazidodichlorosilane, 4086
Diazidodimethylsilane, 0914
* Diphenyl azidophosphate, 3483
Diphenylphosphorus(III) azide, 3482
Disulfuryl diazide, 4774
1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine, 4789
Hydrazinium azide, 4545
Hydrogen azide, 4435
* Lithium tetraazidoborate, 0151
4-Nitrobenzenediazonium azide, 2202

Nitrosyl azide, 4761
* Phosphorus azide difluoride, 4309
* Phosphorus azide difluoride—borane, 4310
Phosphorus triazide, 4783
* Phosphorus triazide oxide, 4782
Silicon tetraazide, 4785
* Sodium hexaazidophosphate, 4788
Sulfinyl azide, 4772
Sulfuryl azide chloride, 4025
Sulfuryl diazide, 4773
* Tetramethylammonium diazidoiodate(I), 1744
Triazidoarsine, 0103
Triazidochlorosilane, 4029
† Trimethylsilyl azide, 1310
See related ACYL AZIDES, HALOGEN AZIDES

NON-METAL HALIDES AND THEIR OXIDES EX_n, EOX_n

This highly reactive class includes the separately treated groups as well as the individually indexed compounds:

Arsenic pentafluoride, 0095
Arsenic trichloride, 0094
* Arsine—boron tribromide, 0101
Bis(*S,S*-difluoro-*N*-sulfimido)sulfur tetrafluoride, 4375
* Bis(trichlorophosphoranylidene)sulfamide, 4182
* Borane—phosphorus trifluoride, 0140
* Boron azide diiodide, 0148
Boron bromide diiodide, 0120
* Boron diiodophosphide, 0149
Boron tribromide, 0122
Boron trichloride, 0127
Boron trifluoride, 0129
* Boron trifluoride diethyl etherate, 1668
Boron triiodide, 0150
* *N*-Carboethoxyiminophosphoryl chloride, 1166
* *N*-Carbomethoxyiminophosphoryl chloride, 0740
Carbonyl dichloride, 0328
* Chloro-1,2,4-triselenadiazolium chloride, 4083
Chlorotetrafluorophosphorane, 3981
Diboron tetrachloride, 0161
Diboron tetrafluoride, 0162
* Dibromoborylphosphine, 0121
* Dichloroborane, 0124
* Dichlorodisilylaminoborane, 0125
* Diethylaminosulfur trifluoride, 1678
Diphosphoryl chloride, 4162

Diselenium dichloride, 4109
Disulfur dibromide, 0281
Disulfur dichloride, 4108
Disulfuryl dichloride, 4097
* Hexachlorocyclotriphosphazine, 4183
Hydriodic acid, 4417
Hydrogen bromide, 0247
Hydrogen chloride, 3987
Hydrogen fluoride, 4288
Krypton difluoride, 4307
* 4-Nitrophenylphosphorodichloridate, 2151
Nitrosyl fluoride, 4296
Nitryl fluoride, 4297
* Pentafluoroorthoselenic acid, 4348
* Phenylphosphonyl dichloride, 2238
* Phosphorus azide difluoride, 4309
* Phosphorus azide difluoride—borane, 4310
Phosphorus chloride difluoride, 3973
* Phosphorus diiodide triselenide, 4624
Phosphorus pentachloride, 4177
Phosphorus tribromide, 0292
Phosphorus trichloride, 4147
* Phosphorus tricyanide, 1339
Phosphorus trifluoride, 4333
Phosphorus triiodide, 4631
Phosphoryl chloride, 4143
* Phosphoryl dichloride isocyanate, 0326
* Poly(dibromosilylene), 0282
* Poly(difluorosilylene), 4324
* Potassium hexafluorosilicate(2—), 4358
Seleninyl bromide, 0274
Seleninyl chloride, 4091
Selenium difluoride dioxide, 4315
Selenium tetrabromide, 0294
Selenium tetrafluoride, 4345
* Silicon dibromide sulfide, 0280
Silicon tetrafluoride, 4346
Sulfinyl bromide, 0273
Sulfinyl chloride, 4090
Sulfinyl fluoride, 4312
Sulfonyl chloride, 4093
Sulfur dibromide, 0279
Sulfur dichloride, 4107
Sulfur hexafluoride, 4368
Sulfur tetrafluoride, 4344
Tellurium tetrachloride, 4169

- * Tetracarbon monofluoride, 1358
- Tetrachlorodiphosphane, 4165
- Tetrachlorosilane, 4167
- Tetraiododiphosphane, 4632
- Thiazyl fluoride, 4300
- * Thiophosphoryl chloride, 4148
- * Thiophosphoryl chloride difluoride, 3974
- * Thiophosphoryl fluoride, 4334
- Thiotrithiazyl chloride, 4027
- Triboron pentafluoride, 0175
- 1,3,5-Trichloro-2,4,6-trifluoroborazine, 0173
- * *B*-1,3,5-Trichloroborazine, 0174
- Trifluoromethanesulfinyl fluoride, 0353
- * Trifluoroselenium hexafluoroarsenate, 0099
- Trifluorosulfur nitride, 4332
- Xenon difluoride, 4326
- Xenon difluoride oxide, 4313
- Xenon hexafluoride, 4371
- Xenon tetrafluoride, 4347

HALOBORANES

N-HALOGEN COMPOUNDS

HALOPHOSPHINES

HALOSILANES

PERFLUOROSILANES

NON-METAL HYDRIDES EH_n

Vogman, L. P., *Chem. Abs.*, 1984, **101**, 116147

The minimum oxygen concentration for explosion of most volatile hydrides of Group IIIA—VA elements is nearly zero, so complete exclusion of air or oxygen is essential for safe working. Presence of impurities in hydride mixtures further increases the danger of ignition.

There are separate group entries below:

Most members of this readily oxidised class ignite in air, individually indexed compounds being:

- † Ammonia, 4492
- * Ammonium hydroxide, 4539
- † Arsine, 0100
- * Arsine—boron tribromide, 0101
- * Borazine, 0176
- * Cobalt tris(dihydrogenphosphide), 4197
- * Dibromoborylphosphine, 0121
- * Dichlorodisilylaminoborane, 0125
- * 1,1-Diethoxy-1,3-disiladioxetane, 1758
- † Hydrazine, 4515
- Hydrogen bromide, 0247

Hydrogen chloride, 3987
† Hydrogen disulfide, 4478
Hydrogen fluoride, 4288
Hydrogen iodide, 4417
† Hydrogen selenide, 4480
† Hydrogen sulfide, 4477
† Hydrogen telluride, 4482
Hydrogen trisulfide, 4479
* Phospham, 4434
† Phosphine, 4503
Silicon monohydride, 4445
‘Solid Phosphorus hydride’, 4443
† Stibine, 4505
‘Unsaturated’ Silicon hydride, 4446

BORANES

PHOSPHINES

SILANES

See related ALKYLNON-METAL HYDRIDES

NON-METAL OXIDES E_mO_n

The generally acidic materials in this group may function as oxidants, some rather powerful, under appropriate conditions. Individually indexed compounds are:

Arsenic pentaoxide, 0106
Arsenic trioxide, 0105
Boron trioxide, 0170
Carbon dioxide, 0554
† Carbon monoxide, 0552
† Carbonyl sulfide, 0553
Deuterium oxide, 4285
Diboron oxide, 0169
Dinitrogen oxide, 4739
Dinitrogen pentaoxide, 4743
Dinitrogen tetraoxide, 4720
Dinitrogen trioxide, 4741
* Diphenylselenone, 3488
Disulfur heptaoxide, 4864
Nitrogen dioxide, 4720
Nitrogen oxide, 4719
* Poly(dihydroxydioxodisilane), 4474
* Potassium hexaoxoxenonate—xenon trioxide, 4669
Selenium trioxide, 4846
Silicon dioxide, 4833
Silicon oxide, 4822
Sulfur dioxide, 4831
Sulfur trioxide, 4843

* Sulfur trioxide—dimethylformamide, 4844
Tellurium trioxide, 4847
* Tetrahydroxydioxotrisilane, 4531
Tetraphosphorus decaoxide, 4866
Tetraphosphorus hexaoxide, 4861
* Tetraphosphorus hexaoxide tetrasulfide, 4863
* Tetraphosphorus hexaoxide—bis(borane), 4862
* Tetraphosphorus tetraoxide trisulfide, 4853
Xenon tetraoxide, 4857
Xenon trioxide, 4851
Xenon(IV) hydroxide, 4528
See GRAPHITE OXIDE, HALOGEN OXIDES

NON-METAL PERCHLORATES $E(ClO_4)_n$

1. Solymosi, F., *Chem. Abs.*, 1972, **77**, 42498
2. Sunderlin, K. G. R., *Chem. Eng. News*, 1974, **52**(31), 3

The thermal stability, structures and physical properties of various non-metal perchlorates (nitrosyl, nitronium, hydrazinium, ammonium, etc.) have been reviewed [1]. Many organic perchlorates were examined for sensitivity to impact. The salts of cations containing only C, H and S exploded quite consistently, while those with C, H, and N, or C, H, N, and S did not explode, except 1,2-bis(ethylammonio)ethane diperchlorate [2]. *See group* and the individually indexed entries:

η-Benzenecyclopentadienyliron(II) perchlorate, 3390
1,3-Benzodithiolium perchlorate, 2673
* 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate, 1583
* Bis(triperchloratosilicon) oxide, 4184
Caesium tetraperchloratoiodate, 4155
1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate, 3382
Chloronium perchlorate, 4059
4,4′-Diphenyl-2,2′-bi(1,3-dithiol)-2′-yl-2-ylium perchlorate, 3740
Diphenylcyclopropenylium perchlorate, 3673
1,3-Dithiolium perchlorate, 1091
Ferrocenium perchlorate, 3263
Fluoronium perchlorate, 3966
(Hydroxy)(oxo)(phenyl)-λ^3-iodanium perchlorate, 2292
Iodine(III) perchlorate, 4134
Nitronium perchlorate, 4022
Nitrosyl perchlorate, 4021
Nitryl perchlorate, 4023
* Peroxypropionyl perchlorate, 1163
Perylenium perchlorate, 3784
Phenyl,phenylethynyliodonium perchlorate, 3628
2-Tetrahydrofuranylidene(dimethylphenylphosphine-trimethylphosphine)-2,4,6-trimethylphenylnickel perchlorate, 3848

2-Tetrahydropyranylidene-bis(dimethylphenylphosphine)-3,4,6-trimethylphenyl-nickel perchlorate, 3871
2,3,4,6-Tetramethylpyrilium perchlorate, 3161
Tetraperchloratosilicon, 4163
Thianthrenium perchlorate, 3449
Thiotrithiazyl perchlorate, 4026
Triferrocenylcyclopropenium perchlorate, 3879
2,4,6-Trimethylpyrilium perchlorate, 2987
Trimethylsilyl perchlorate, 1298
2,4,6-Triphenylpyrilium perchlorate, 3833
Tris(ethylthio)cyclopropenium perchlorate, 3173
* 1,4,7-Trithia[7]ferrocenophene—acetonitrilecopper(I) perchlorate, 3704
Tropylium perchlorate, 2738
Xenon(II) fluoride perchlorate, 3971

Trifluoromethanesulfonic acid

Several perchlorate derivatives of non-metallic elements (including some non-nitrogenous organic compounds) are noted for explosive instability.

See Trifluoromethanesulfonic acid: Perchlorate salts
ALKENEBIS(SULFONIUM PERCHLORATES)
ORGANOSILYL PERCHLORATES
PERCHLORATE SALTS OF NITROGENOUS BASES
PERCHLORATE-DOPED CONDUCTING POLYMERS
See other PERCHLORATES

NON-METALS E

Some members of this group of elements are readily oxidised with more or less violence dependent upon the oxidant and conditions of contact. Individually indexed elements (and some binary compounds) are:

Argon, 0091
Arsenic, 0092
Boron, 0119
* Boron nitride, 0152
* Boron phosphide, 0156
Carbon, 0297
* Carbon tetraboride, 0308
† Hydrogen (Gas), 4447
† Hydrogen (Liquid), 4448
Nitrogen (Gas), 4729
Nitrogen (Liquid), 4730
Oxygen (Gas), 4825
Oxygen (Liquid), 4826
Ozone, 4840
† Phosphorus, 4868

* Selenium, 4902
* Silicon, 4903
† Sulfur, 4891
* Tellurium, 4910
Xenon, 4920

NON-METAL SULFIDES E_mS_n

In this group of readily oxidised materials, individually indexed compounds are:
Arsenic trisulfide, 0108
Bis(2,4-dinitrophenyl) disulfide, 3443
Bis(2-nitrophenyl) disulfide, 3459
Boron trisulfide, 0172
† Carbon disulfide, 0557
Carbon sulfide, 0556
† Carbonyl sulfide, 0553
* Disilyl sulfide, 4563
† Hydrogen disulfide, 4478
† Hydrogen selenide, 4480
† Hydrogen sulfide, 4477
Hydrogen trisulfide, 4479
* Phosphorus diiodide triselenide, 4624
Propadienedithione, 1346
* Silicon dibromide sulfide, 0280
Silicon monosulfide, 4892
Tetraarsenic tetrasulfide, 0109
* Tetramethyldiphosphane disulfide, 1760
Tetraphosphorus decasulfide, 4872
* Tetraphosphorus decasulfide . pyridine complex, 4873
* Tetraphosphorus hexaoxide tetrasulfide, 4863
* Tetraphosphorus tetraoxide trisulfide, 4853
* Tetraphosphorus triselenide, 4874
Tetraphosphorus trisulfide, 4871
* Tris(2-propylthio)phosphine, 3216

N—S COMPOUNDS N—S

Bojes, J. *et al., Inorg. Synth.*, 1989, **25**, 30

Many compounds containing either single or multiple bonds between N and S show a considerable degree of instability. Information is given on hazards of, and precautions in handling derivatives of cyclic N-S compounds [1]. Individually indexed compounds are:
Amidosulfuric acid, 4494
5-Amino-1,2,3,4-thiatriazole, 0412
* Ammonium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide, 4586
* Ammonium amidoselenate, 4552
Ammonium amidosulfate, 4551

* Ammonium thiosulfate, 4568
Benzo-1,2,3-thiadiazole, 2192
Benzo-1,2,3-thiadiazole 1,1-dioxide, 2184
3,4-Bis(1,2,3,4-thiatriazol-5-ylthio)maleimide, 2066
Bis(1,2,3,4-thiatriazol-5-ylthio)methane, 1081
Bis(dimethylamino) sulfoxide, 1751
Bis-*N*(imidosulfurdifluoridato)mercury, 4336
Bis(*S,S*-difluoro-*N*-sulfimido)sulfur tetrafluoride, 4375
* Bis(trichlorophosphoranylidene)sulfamide, 4182
* Carbonyl(pentasulfur pentanitrido)molybdenum, 0532
5-Chloro-1,2,3-thiadiazole, 0651
* Chloro-1,2,4-triselenadiazolium chloride, 4083
(Chlorocarbonyl)imidosulfur difluoride, 0317
* Chlorosulfonyl isocyanate, 0323
Cyclopentaazathienium chloride, 4028
1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3386
N,N-Dichloropentafluorosulfanylamine, 4054
S-Diethylamino(methylimino)sulfur(IV) fluoride, 2021
Diethylaminosulfinyl chloride, 1673
Diethylaminosulfur trifluoride, 1678
S,S-Dimethylpentasulfur hexanitride, 0913
* 2,2-Diphenyl-1,3,4-thiadiazoline, 3640
Diseleniumdisulfur tetranitride, 4763
Disulfur dinitride, 4749
* Disulfur thiocyanate, 0999
Ethyl 4-bromo-1,1,3-trioxoisothiazoleacetate, 2788
Ethyl 6-ethoxycarbonyl-3,4-dihydro-1,1,3-trioxo-2-pyrazolo[3,4-d]isothiazole-2-acetate, 3397
N-Fluoroiminosulfur tetrafluoride, 4351
5-Hydrazino-1,2,3,4-thiatriazole, 0461
Iodinated poly(sulfur nitride), 4617
Mercury(I) thionitrosylate, 4605
4-Morpholinesulfenyl chloride, 1581
4,4′-Oxybis(benzenesulfonylhydrazide), 3519
Pentamethylcyclopentadienyl-bis(thiolatothiatriazyl)rhodium, 3528
Pentasulfur hexanitride, 4778
N-Phenyl-1,2,3,4-thiatriazolamine, 2725
* Poly(selenium nitride), 4725
Poly(sulfur nitride), 4723
Potassium 4-nitrobenzeneazosulfonate, 2168
* Potassium azodisulfonate, 4658
Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, 4657
Potassium sulfurdiimidate, 4659
Potassium thiazate, 4643
5-(Prop-2-ynyloxy)-1,2,3,4-thiatriazole, 1416
* Seleninyl bis(dimethylamide), 1752

Silver trisulfurpentanitridate, 0024
Sodium tetrasulfur pentanitridate, 4769
Sodium trisulfurtrinitridate, 4755
Sulfinylcyanamide, 0539
Sulfur oxide-(*N*-fluorosulfonyl)imide, 4299
* Sulfur thiocyanate, 0998
* Tetraselenium dinitride, 4751
* Tetraselenium tetranitride, 4765
Tetrasulfur dinitride, 4750
Tetrasulfur tetranitride, 4764
* Tetrasulfurtetraimide—silver perchlorate, 0029
* Tetratellurium tetranitride, 4767
Thiazyl fluoride, 4300
Thiotrithiazyl chloride, 4027
Thiotrithiazyl nitrate, 4762
Thiotrithiazyl perchlorate, 4026
2-Thioxo-4-thiazolidinone, 1109
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine, 4139
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum, 4136
N-(Trifluoromethylsulfinyl)trifluoromethylimidosulfinyl azide, 0636
Trifluorosulfur nitride, 4332
Tris(thionitrosyl)thallium, 4759
See also *N*-HALOGEN COMPOUNDS

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14. Nazin, E. R. *et al., Chem. Abs.*, 2004, **140**, 361886e
15. Yoneya, M. et al., Chem. Abs., 2000, 133, 50004q

There are chemical explosion hazards associated with stored reprocessing residues. The explosion near Chelyabinsk in the Urals in 1958 was, it has been suggested, powered by interaction of sodium nitrate and/or nitric acid with sodium acetate/acetic acid in nitrate wastes neutralised with sodium acetate, then stored and allowed to concentrate by radioactive heating [1]. A reprocessing incident at Tomsk in 1993 was apparently caused by adding nitric acid to an inadequately stirred tank of actinide salts, mostly uranium, with a butyl phosphate/paraffin extraction solvent. The substantial explosion was probably caused by nitric acid oxidation of the organics [2]. Explosive 'red oils', apparently organic nitrate by-products, are a hazard of such processing [6]. Experiment shows that, when heated above 160°C with nitric acid or metal nitrates, (tri)butyl phosphate generates gas mixtures which can autoignite. Pressures of tens of bars may be generated. It is suggested that this mechanism explains some reprocessing explosions [7]. The calorimetric and explosive characteristics of such mixtures have been described by Japanese workers [9]. A Russian study of the reaction between tributyl phosphate and nitric acid in organic media, defining safety limits and giving kinetic data for dangerous reactions, is also available [10]. Not surprisingly, butyl phosphate becomes more sensitive in presence of ionising radiation [14]. Procedures for removing nitric acid from wastes by controlled reaction with formic acid have been developed [11]. A study of the risks with nitrate residues containing ferrocyanide as fuel has been published [3]. Explosions from extremely prolonged storage of nitric acid and hydroxylamine solutions, with and without hydrazine, which are used as reagents in reprocessing are also reported. Initial concentration by evaporation seems to be involved [8].

A fire and explosion reulted from encapsulating nuclear waste [15], consisting mostly of sodium nitrate, in asphalt. The full details of the reaction reported are complex, the principles simple [12]. Nitrate/asphalt has previously seen application as rocket fuel and may have been behind Greek Fire [Editor]. A more theoretical study, also looking at the influence of silver compounds has appeared [13].

Gas evolution, by radiation induced dissociation of water and other components, can also permit build-up of pressure behind crusts forming on evaporation of solvent; should the hydrogen peroxide also formed from water later decompose, the gas produced could be an explosive mixture of hydrogen and oxygen. Alkaline reprocessing wastes containing ethylenediamine tetracetic acid (EDTA) evolve large volumes of hydrogen. It is postulated that this is by radiation cleavage of EDTA to formaldehyde, which is shown to produce hydrogen chemically when at low concentrations in aqueous alkali [4].

For a general consideration of largely chemical reaction hazards of concentrated wastes [5].

See Formaldehyde, Nitric acid
See Hydroxylaminium nitrate
See also IRRADIATION DECOMPOSITION INCIDENTS

OLEUM (FUMING SULFURIC ACID) **$H_2SO_4.SO_3$**

See Sulfur trioxide: Sulfuric acid

ORGANIC ACIDS **RCO.OH, $ArSO_2.OH$, ArOH, etc.**

This group has examples of many types of acids derived from aliphatic, aromatic and heterocyclic radicals, with carboxylic, phenolic or sulfonic or related functional substituents. Individually indexed acids are:

Acetic acid, 0829
1-Acetyl-4-(4′-sulfophenyl)-3-tetrazene, 2977
Acetylenedicarboxylic acid, 1401

O-Acetylsalicylic acid, 3131
Acrylic acid, 1145
Adipic acid, 2435
Azelaic acid, 3181
Azidoacetic acid, 0770
Azidodithioformic acid, 0385
Benzeneseleninic acid, 2328
Benzeneselenonic acid, 2331
Benzoic acid, 2728
Bis(3-carboxypropionyl) peroxide, 2985
4-Bromomethylbenzoic acid, 2921
Butyric acid, 1609
* 2-Carboxy-3,6-dimethylbenzenediazonium chloride, 3132
* *S*-Carboxymethylisothiouronium chloride, 1241
2-Chloro-5-nitrobenzenesulfonic acid, 2137
Citric acid, 2383
Citronellic acid, 3346
Cyanoacetic acid, 1110
Diazirine-3,3-dicarboxylic acid, 1077
Diazomalonic acid, 1078
2,2-Dibromo-1,3-dimethylcyclopropanoic acid, 2357
N,N-Dichloroglycine, 0735
Difluoroacetic acid, 0698
Dihydroxymaleic acid, 1443
3,5-Dimethylbenzoic acid, 3146
2,5-Dinitro-3-methylbenzoic acid, 2914
* Ferrocene-1,1′-dicarboxylic acid, 3472
Formic acid, 0417
Fumaric acid, 1442
Glyoxylic acid, 0720
2,4-Hexadienoic acid, 2379
2,4-Hexadiyne-1,6-dioic acid, 2087
2-Hydroxy-2-methylglutaric acid, 2439
4-Hydroxy-3,5-dinitrobenzenearsonic acid, 2213
4-Hydroxy-*trans*-cinnamic acid, 3130
N-Hydroxydithiocarbamic acid, 0453
1-Hydroxyethylidene-1,1-diphosphonic acid, 0952
2-Iodylbenzoic acid, 2677
Lactic acid, 1230
Methacrylic acid, 1525
Methanesulfonic acid, 0486
4-Methyl-3-nitrobenzenesulfonic acid, 2769
2-Methyl-5-nitrobenzenesulfonic acid, 2768
4-Nitroaniline-2-sulfonic acid, 2312
3-Nitrobenzenesulfonic acid, 2261
2-Nitrobenzoic acid, 2689

3-Nitrobenzoic acid, 2690
4-Nitrobenzoic acid, 2691
2-(4-Nitrophenoxyazo)benzoic acid, 3595
* 3-(2-Nitrophenyl) -2-hydroxyiminopropanoic acid, 3125
2-Nitrophenylpropiolic acid, 3107
3-Nitrophthalic acid, 2901
Nitroterephthalic acid, 2902
9,12,15-Octadecatrienoic acid, 3765
cis-9-Octadecenoic acid, 3768
Octatetrayne-1,8-dicarboxylic acid, 3229
Oxalic acid, 0721
Pentanesulfonic acid, 2014
Perfluorosuccinic acid, 1387
3-Peroxycamphoric acid, 3342
Phthalic acid, 2918
Picric acid, 2111
* Potassium hydrogen acetylenedicarboxylate, 1378
* Potassium hydrogen tartrate, 1458
E-Propene-1,2,3-tricarboxylic acid, 2335
Propiolic acid, 1083
2,5-Pyridinedicarboxylic acid, 2692
Pyruvic acid, 1147
Tartaric acid, 1540
Terephthalic acid, 2919
† Thiolacetic acid, 0828
4-Toluenesulfonic acid, 2804
Trichloroacetic acid, 0654
Trifluoroacetic acid, 0661
Trifluoromethanesulfonic acid, 0374
Trinitroresorcinol, 2112

ORGANIC AZIDES RN_3, ArN_3

1. Boyer, J. H. *et al., J. Chem. Eng. Data*, 1964, **9**, 480; *Chem. Eng. News*, 1964, **42**(31), 6
2. Draper, R. W., *J. Chem. Soc., Perkin Trans. I*, 1983, 2787
3. Scheri, S. H. *et al., J. Mol. Struct.*, 1986, **14**7, 203—204
4. Petrie, M. A. *et al., J. Amer. Chem. Soc.*, 1997, **119**, 8802
5. Stadlbauer, W. *et al., J. Biochem & Biophys. Methods*, 2002, 53(1), 89

The need for careful and small-scale handling of organic azides, which are usually heat- or shock-sensitive compounds of varying degrees of stability, sensitive to traces of strong acids and metallic salts which may catalyse explosive decomposition, has been discussed. The presence of more than one azido group, particularly if on the same atom (C or N), greatly reduces the stability [1]. Two reaction systems used to prepare steroidal azides are potentially dangerous, and should only be used with extensive safety precautions. The first involves use of chromium trioxide, sodium azide and acetic acid, and is likely to produce chromyl azide and hydrazoic acid, both explosive. The second uses lead(IV) acetate and trimethylsilyl azide and could produce lead azide. Use of remote control handling equipment is recommended [2]. Unsaturated azides containing one or more double or triple bonds, and one or more azide groups, are particularly dangerous, and should be handled with the utmost care [3]. Not surprisingly, all salts of the triazido carbenium ion (N_9C+) were found to be sensitive explosives, the perchlorate was the most sensitive, the dinitramide the most powerful [4].

A range of heterocyclic azides were studied by differential scanning calorimetry, the enthalpies of thermal decomposition were lower than might have been expected, from 0.3—1 kJ/g. If ortho substituents onto which the azide could cyclise were present, decomposition enthalpies were, as one would expect, lower still [5].

as well as the individually indexed compounds:

3-Azido-1,2,4-triazole, 0713
2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate, 3460
Azido-2-butyne, 1469
2-Azido-2-phenylpropane, 3154
2-Azido-3,5-dinitrofuran, 1380
Azidoacetonitrile, 0710
Azidoacetyl chloride, 0689
4-Azidobenzaldehyde, 2693
7-Azidobicyclo[2.2.1]hepta-2,5-diene, 2773
* *N*-Azidodimethylamine, 0911
2-Azidoethanol, 0869
6-Azidohexyl 6-azidohexanoate, 3545
2-Azidomethylbenzenediazonium tetrafluoroborate, 2704
4-Azido-*N,N*-dimethylaniline, 3325
2-Azidoperfluoronaphthalene, 3228
3-Azidopropene, 1184
3-Azidopropyne, 1111
5-Azidotetrazole, 0387
Benzyl azide, 2775
* Bis(2-azidobenzoyl) peroxide, 3621
1,2-Bis(2-azidoethoxy)ethane, 2473
Bis(2-azidoethoxymethyl)nitramine, 2475
3,3-Bis(azidomethyl)oxetane, 1896
N-Butyl-*N*-2-azidoethylnitramine, 2523
2,3-Diazido-1,3-butadiene, 1433
1,2-Diazido-1-phenylethane, 2949
1,3-Diazido-2-nitroazapropane, 0820
1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane, 3044
2,4-Diazido-6-dimethylamino-1,3,5-triazine, 1870
1,3-Diazidobenzene, 2200
1,4-Diazidobenzene, 2201
1,1-Diazidoethane, 0814
1,2-Diazidoethane, 0815
Diazidomalononitrile, 1343

Diazidomethane, 0413
Diazidomethyleneazine, 1017
Diazidomethylenecyanamide, 1013
1,1-Diazidophenylethane, 2948
2,2-Diazidopropane, 1212
1,3-Diazidopropene, 1140
2,3-Diazidopropiononitrile, 1118
2,6-Diazidopyrazine, 1396
3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2397
Ethyl 2,3-diazidopropionate, 1897
Ethyl azide, 0868
* 1-Ferrocenyl-2-methylpropyl azide, 3654
Fluorodinitromethyl azide, 0340
Glycidyl azide, 1187
Methyl 2-azidobenzoate, 2934
Methyl 3,3-diazido-2-cyanoacrylate, 1818
Methyl azide, 0458
1,1′-Oxybis-2-azidoethane, 1599
Phenyl azide, 2264
Phenyldiazidomethane, 2726
2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile), 3616
I-Phenyl-*I*-(*p*-toluenesulfonyloxy)-(2-azido-2-phenyl)vinyliodine(III), 3815
Picryl azide, 2085
Silver 2-azido-4,6-dinitrophenoxide, 2068
* Thiocarbonyl azide thiocyanate, 1007
2,4,6-Triazido-1,3,5-triazine, 1344
1,1,1-Triazidodinitroethane, 0679
Triazidomethane, 0388
* Triazidomethylium hexachloroantimonate, 0334
Trifluoromethyl azide, 0346
Triphenylmethyl azide, 3777
Tris(2-azidoethyl)amine, 2476
1,1,1-Tris(azidomethyl)ethane, 1931
Vinyl azide, 0766
ACYL AZIDES
2-AZIDOCARBONYL COMPOUNDS
See related NON-METAL AZIDES

ORGANIC BASES

The separately treated METAL ALKOXIDES may perhaps be regarded as organic bases, as well as the more conventional nitrogenous bases below:

1-Amino-2-propanol, 1307
Aminoguanidine, 0504
Benzylamine, 2808
Benzyldimethylamine, 3162

N,N′-Bis(2-aminoethyl)1,2-diaminoethane, 2595
Bis(2-aminoethyl)amine, 1771
Bis(2-fluoro-2,2-dinitroethyl)amine, 1455
† 1,2-Bis(dimethylamino)ethane, 2574
† Butylamine, 1717
† 2-Butylamine, 1718
† Butylethylamine, 2563
† Cyclohexylamine, 2516
† Cyclopentylamine, 1985
† Di-2-butylamine, 3078
† Diallylamine, 2444
1,11-Diamino-3,6,9-triazaundecane, 3095
1,4-Diaminobenzene, 2364
1,2-Diaminoethane, 0949
† 1,2-Diaminopropane, 1321
† 1,3-Diaminopropane, 1322
1,4-Diazabicyclo[2.2.2]octane, 2467
Dibutylamine, 3077
3-Dibutylaminopropylamine, 3410
† Diethylamine, 1720
3-Diethylaminopropylamine, 2872
† Diisobutylamine, 3079
† Diisopropylamine, 2561
3,3′-Dimethoxy-4,4′-diaminobiphenyl, 3653
† Dimethylamine, 0937
(Dimethylamino)acetylene, 1559
† 2-Dimethylaminoethylamine, 1749
N,N-Dimethylaniline, 2988
† 1,3-Dimethylbutylamine, 2562
† 1,2-Dimethylhydrazine, 0951
† 2,6-Dimethylpiperidine, 2863
† 2,2-Dimethylpropylamine, 2024
† 1,2-Dimethylpropylamine, 2023
† 1,1-Dimethylpropylamine, 2022
† *N,N*-Dimethylpropylamine, 2025
† Dipropylamine, 2563
5-Ethyl-2-methylpyridine, 2990
† Ethylamine, 0938
† Ethyldimethylamine, 1721
† 1-Ethylpiperidine, 2864
† 2-Ethylpiperidine, 2865
Hexamethylenetetramine, 2471
N-2-Hydroxyethyl-1,2-diaminoethane, 1750
2-Hydroxyethylamine, 0939
N-2-Hydroxyethyldimethylamine, 1723
† Isobutylamine, 1722

† Isopentylamine, 2026
† Isopropylamine, 1304
† Methylamine, 0491
† *N*-Methylbutylamine, 2027
† Methylhydrazine, 0500
† 4-Methylmorpholine, 1989
† 1-Methylpiperidine, 2517
† 2-Methylpiperidine, 2518
† 3-Methylpiperidine, 2519
† 4-Methylpiperidine, 2520
2-Methylpyridine, 2348
† *N*-Methylpyrrolidine, 1986
Morpholine, 1652
† Pentylamine, 2028
† Perhydroazepine, 2521
Phenylhydrazine, 2366
N-Phenylhydroxylamine, 2349
Piperazine, 1683
† Piperidine, 1987
† Propylamine, 1305
† Pyridine, 1842
Quinoline, 3115
† 1,2,3,6-Tetrahydropyridine, 1924
1,3,4,7-Tetramethylisoindole, 3522
1,2,4,5-Tetrazine, 0711
Thiourea, 0478
3,6,9-Triaza-11-aminoundecanol, 3094
1,3,5-Triazine, 1112
† Triethylamine, 2564
† Trimethylamine, 1306
2,4,6-Tris(dimethylaminomethyl)phenol, 3687
Tris(hydroxymethyl)methylamine, 1725
Urea, 0474
Vinylpyridine, 2755

ORGANIC ISOCYANATES RN=C=O

Mumford, C. J. *et al., Loss Prev. Bull.*, 1991, **102**, 7

These high energy species are extremely reactive, with themselves and with nucleophiles, and can generate runaway exotherms. With water, rapid evolution of carbon dioxide results. Some instances are reported [1]. A compound of this class was responsible for Bhopal, the worst chemical industry accident to date. Di-isocyanates are extensively employed, with polyols, to generate polyurethane polymers. The polymerisation temperature should be held below 180°C or decomposition may occur which, in the case of foams, may induce later autoignition.

Individually indexed compounds are:
- Butane-1,4-diisocyanate, 2369
- † Butyl isocyanate, 1925
- 4-Chlorophenyl isocyanate, 2644
- 1,6-Diisocyanatohexane, 3003
- Diisocyanatomethane, 1076
- 2,4-Diisocyanatotoluene, 3111
- † Methyl isocyanate, 0758
- 1-Naphthyl isocyanate, 3384
- Phenyl isocyanate, 2681
- 2-Phenylethyl isocyanate, 3133
- * Trifluoromethyliodine(III) isocyanate, 1042

See Potassium cyanate

ORGANIC PEROXIDES C—OO

1. Noller, D. C. *et al., Anal. Chem.*, 1963, **35**, 887—893
2. Castrantas, 1970
3. Varjarvandi, J. *et al., J. Chem. Educ.*, 1971, **48**, A451
4. *Code of Practice for Storing and Handling of Organic Peroxides*, P15.1, Luton, Interox Chemicals, 1975
5. *Storage and Handling of Organic Peroxides*, Guidance Note CS 21, HMSO, London.
6. Jackson, H. L., *J. Chem. Educ.*, 1970, **47**, A175
7. Castrantas, 1965
8. Davies, 1961
9. Swern, 1970, Vol. 1, 1—104
10. Houben-Weyl, 1952, Vol. 8.3, 1
11. Swern, 1972, Vol. 3, 341—364
12. Stevens, H. C., US Pat. 2 415 971, 1947
13. Cookson, P. G. *et al., J. Chem. Soc., Chem. Comm.*, 1976, 1022—1023
14. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 32
15. Kotani, M. *et al., Chem. Abs.*, 1980, **92**, 87594
16. Marisaki, S., *Chem. Abs.*, 1983, **98**, 34100
17. Matsunaga, T. *et al., Chem. Abs.*, 1984, **101**, 113378
18. Halle, R., *Chem. Eng. News*, 1984, **62**(47), 4
19. Tamura, M. *et al., J. Haz. Mat.*, 1987, **17**(1), 89—98
20. Mackenzie J., *Plant/Oper. Progr.*, 1991, **10**(3), 165
21. Anon., *Jahresber.*, 1987, 65
22. Schammler, S. *Chem. Anlagen Verfahren*, 2001, **34**(5), 22
23. Bosch, C. M. *et al., Chem. Eng. Sci.*, 2001, **56**(4), 1451

Of the general guides to the safe handling and use of peroxides, the third and second include details of hazard evaluation tests, and the first has a comprehensive bibliography [1,2,3]. Storage aspects are rather specific [2,4]. Appropriate means for the refrigerated storage of low tonnage quantities of organic peroxides have been described [22]. Procedures for the safe handling of peroxidisable compounds have also been described [5]. Tabulated data on fire and explosion hazards of classes of organic peroxides with an extensive bibliography were published [6]. Theoretical aspects have been considered [6,7,8], the practical hazards involved in synthesis of organic peroxides have been detailed [9], and a further review on the evaluation and management of peroxide hazards appeared [10]. The use of iodine to stabilise liquid organic peroxides against explosive or incendiary decomposition has been claimed [11]. A new safe general method for rapid preparation of n-, *sec*- or *tert*-alkyl hydroperoxides has been described [12]. Leakage of an organic peroxide catalyst solution into pipe lagging exposed to direct solar radiation led to a fire [13].

Pyrolysis GLC has been used to develop a safe method for the qualitative determination of thermally unstable organic peroxides like benzyl peroxide. The mechanism of decomposition reactions and the temperature limits for safe handling of peroxides can also be determined by this technique [14]. In a study of adiabatic thermal decomposition, 2 g samples of di-*tert*-butyl and dibenzoyl peroxides, *tert*-butyl peroxybenzoate and peroxy-2-ethylhexanoate attained maximum self-heating rates and final pressures of 150—440°C/min and 4.5—9.5 kbar, respectively [15]. Group contributions to heat of formation (l) were derived from suitable reference compounds and used to estimate ΔH_f° for peroxides by additivity methods. The agreement between calculated and observed values were good enough to estimate hazard properties for energetic materials such as peroxides [16]. A general measure of the degree of hazard associated with an organic peroxide may be gained from the content of 'active oxygen' (AO, or wt% of peroxidic oxygen) in the molecule. Thus 2,2-bis(hydroperoxy)propane (highly explosive) with 30.2% AO has an extremely high value compared to the 1—17% commonly encountered in commercial organic peroxides, e.g. MEK peroxide, which is supplied and handled safely as a solution diluted to a maximum AO content of 9% [17].

Work on the deflagration hazards of organic peroxides has been done using a revised Time—Pressure test, to determine the characteristics of ignition sensitivity and violence of deflagration. Some correlation is evident between these characteristics and the AO content within each structurally based peroxide type. Also, for the same AO content, the nature of the characteristics appears to decrease in the order diacyl peroxides, peroxyesters, dialkyl peroxides, alkylhydroperoxides [18]. Semi-empirical methods for calculating self-accelerating runaway conditions for organic peroxides and solutions thereof have been described [23].

Warning is given that sodium sulfite may not remove all peroxidic compounds if peroxyacids are present, with which it can form undetectable, but unstable, complex peroxides [19]. Peroxide test strips may not be sufficiently reliable as the sole means of testing for presence of peroxides in a wide range of peroxidisable liquids. It was recommended that an additional test (potassium iodide—acetic acid) should be used unless it is certain that the test strips will give a positive result with a particular peroxide-containing liquid [20].

Except for the peroxides individually listed below, all index entries have been assigned to the structurally based groups:
Individually indexed compounds are:

- ∗ Chloroperoxytrifluoromethane, 0318
- ∗ Perfluoro-*tert*-butyl peroxyhypofluorite, 1369
- ∗ Peroxypropionyl perchlorate, 1163
- ∗ 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3H)pyrazole, 3835

ALKYL HYDROPEROXIDES
tert-BUTYL PEROXOPHOSPHATE DERIVATIVES
CYCLIC PEROXIDES
DIACYL PEROXIDES
DIALKYL PEROXIDES
DIOXETANES
KETONE PEROXIDES
1-OXYPEROXY COMPOUNDS
OZONIDES
PEROXYACIDS
PEROXYCARBONATE ESTERS
PEROXYESTERS
α-PHENYLAZO HYDROPEROXIDES
POLYPEROXIDES
See also COMMERCIAL ORGANIC PEROXIDES

ORGANIC POWDER HANDLING

1. *Electrostatic hazards in powder handling*, Gior, M., Letchworth, Research Study Press, 1988 (also from Wiley)

The role of electrostatic generation as an important ignition source in industrial powder handling operations is discussed in this book.
See DUST EXPLOSION INCIDENTS, ELECTROSTATIC HAZARDS, IGNITION SOURCES

ORGANOLITHIUM REAGENTS XArLi

1. Bretherick, L., *Chem. & Ind.*, 1971, 1017
2. Gilman, H., private comm., 1971
3. ‘Benzotrifluorides Catalog 6/15’, West Chester (Pa.), Marshallton Res. Labs., 1971
4. Coates, 1960, 19
5. *MCA Case History No. 1834*
6. Anderson, R., *Chem. & Ind.*, 1984, 205208
7. Wakefield, B. J., *Organolithium Methods*, London, Academic, 1988

Several halo-aryllithium compounds are explosive in the solid state in absence or near-absence of solvents or diluents, and operations should be designed to avoid their separation from solution. Such compounds include *m*- and *p*-bromo-, *m*-chloro-, *p*-fluoro-, *m*- and *p*-trifluoromethyl-phenyllithiums [1] and 3,4-dichloro-2,5-dilithiothiphene [2], but *m*-bromo- and *o*-trifluoromethyl-phenyllithium appear to be explosive in presence of solvent also [1,3]. The *m*- and *p*-dilithiobenzenes are also explosively unstable under certain conditions. Most organolithium compounds are pyrophoric when pure (especially those of high lithium content) and are usually handled in solution and under inert atmosphere [4]. A completed preparation of *o*-trifluoromethylphenyllithium refluxing in ether under nitrogen suddenly exploded violently [5]. Equipment and procedures necessary for the safe use of organolithium reagents on the industrial scale have been detailed [6]. Aspects of practical significance (solvents, inert atmospheres, equipment, and handling procedures) related to the safe use of organolithium reagents are included in the volume [7].

Examples of these compounds may be found in the group and the individual entries:

4-Bromophenyllithium, 2123
3-Bromophenyllithium, 2122
4-Chlorophenyllithium, 2132
3-Chlorophenyllithium, 2131
3,4-Dichloro-2,5-dilithiothiophene, 1353
1,4-Dilithiobenzene, 2172
1,3-Dilithiobenzene, 2171
4-Fluorophenyllithium, 2159
2-,3- or 4-Trifluoromethylphenyllithium, 2651

FLUORINATED ORGANOLITHIUM COMPOUND
See other HALO-ARYLMETALS

ORGANOMETALLIC NITRATES

These compounds, although not as dangerous as the related perchlorates, have a reducing organic moiety in intimate association with an oxidant nitrate, combined with a metal which may well be an oxidation catalyst. They feature increasingly as explosive compounds in reports too numerous to feature all as individual entries in a handbook. These comments apply equally to the complexed species loosely described as organometallic although lacking a carbon—metal bond. Individual compounds include:

η^6-Benzeneruthenium(II) dinitrate, 2313
Dimethyltin dinitrate, 0910
2-Hydroxyethylmercury(II) nitrate, 0853
2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1587
See AMMINEMETAL OXOSALTS, METAL NITRATES

ORGANOMETALLIC PERCHLORATES

The comments on organometallic nitrates, above, apply with redoubled force here. Although becoming fewer as chemists learn caution, reports of explosion are even more numerous than for the nitrates, and the explosions are more powerful. Again far from all reported have been given entries. Individual compounds are:
See AMMINEMETAL OXOSALTS, METAL PERCHLORATES, PERCHLORATES

ORGANOMETALLIC PEROXIDES RM—OO, RE—OO

1. Castrantas, 1965, 18
2. Swern, 1970, Vol. 1, 13
3. Sosnovsky, G. *et al., Chem. Rev.*, 1966, **66**, 529
4. Colletti, S. L. *et al., J. Organomet. Chem.*, 1993, **455**(1-2), 99

Available information suggests that both hydroperoxides and peroxides in this extensive group of compounds are in many cases stable to heat at temperatures rather below 100°C, but may decompose explosively at higher temperatures. There are, however, exceptions [1]—[3]. Organoniobium peroxides may be explosive when exposed to air [4]. Individually indexed compounds are:

* Bis(methylcyclopentadienyl)peroxoniobium chloride, 3516
Bis(triethyltin) peroxide, 3575
Dicyclopentadienylperoxyniobium chloride, 3265
Diethylhydroxytin hydroperoxide, 1757
Di(hydroperoxy)trimethylantimony(V), 1329
Methylbis(η^2-peroxo)rhenium oxide hydrate, 0494
Triethyltin hydroperoxide, 2578
Trimethylsilyl hydroperoxide, 1326
Triphenyltin hydroperoxide, 3752
See also ALKYL TRIALKYLLEAD PEROXIDES

ORGANOMETALLICS C—M

High Energy Processes in Organometallic Chemistry, Suslick, K. S. (ed.), ACS Symp. Ser. No 333, Washington, ACS, 1987

Several of the chapters in this 336 page book are concerned with the preparation, properties and use of very highly reactive materials in organometallic chemistry.

This class of rather miscellaneous organometallic compounds, all with carbon—metal bonding, contains the separately treated groups and the individually indexed compounds:

* Benzylsodium, 2783
* Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum] —tetrakis(tetrahydrofuran)magnesium, 3829
* Bis(2,4-pentanedionato)chromium, 3320
Bis(benzene)chromium dichromate, 3845
Bis(benzeneiron)—fulvalenediyl complex, 3828
Bis(cycloctatetraene)uranium(0), 3701
Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, 3824
Bis(cyclopentadienyldinitrosylchromium), 3269
Bis(cyclopentadienyl)hexafluoro-2-butynechromium, 3629
Bis(cyclopentadienyl)lead, 3288
Bis(cyclopentadienyl)magnesium, 3271
Bis(cyclopentadienyl)manganese, 3272
Bis(cyclopentadienyl)niobium tetrahydroborate, 3318
* Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide, 3696
* Bis(cyclopentadienyl)phenylvanadium, 3698

Bis(cyclopentadienyl)titanium, 3289
Bis(cyclopentadienyl)titanium selenate, 3287
Bis(cyclopentadienyl)zirconium, 3290
Bis(dicarbonylcyclopentadienyliron)—bis(tetrahydrofuran)magnesium, 3829
Bis(pentafluorophenyl)ytterbium, 3417
* Bis(η-benzene)chromium(0), 3505
* Bis(η-benzene)iron(0), 3506
* Bis(η-benzene)molybdenum(0), 3508
Bis(μ_3-methylidyne)*triangulo*tris(pentamethylcyclopentadienylrhodium), 3907
Chloro(η^8 1,3,5,7-cyclooctatetraene)(tetrahydrofuran)lutetium, 3530
* (η^8 1,3,5,7-Cyclooctatetraene)[2-(dimethylaminomethyl)phenyl-*C,N*](tetrahydrofuran)lutetium, 3820
μ-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino)titanium, 3023
Cyclopentadienylsodium, 1849
μ-Cyclopentadienyltrimethyltitanium, 3033
1,3-Di[bis(cyclopentadienyl)iron]-2-propen-1-one, 3834
Diaquabis(cyclopentadienyl)titanium dichromate, 3321
cis-Dicarbonyl(cyclopentadienyl)cyclooctenemanganese, 3682
* Dicarbonyl-π-cycloheptatrienyltungsten azide, 3117
* (2,2-Dichloro-1-fluorovinyl)ferrocene, 3463
Dicumenechromium(0), 3761
Dicyclopentadienylchromium, 3267
4,4-Diferrocenylpentanoyl chloride, 3853
Dilithium μ-cyclooctatetraene, 2943
Dimethylaminomethylferrocene, 3607
2-(Dimethylaminomethyl)fluoroferrocene, 3606
Dipotassium μ-cyclooctatetraene, 2942
Ferrocene, 3270
* Ferrocene-1,1′-dicarboxylic acid, 3472
* 1-Ferrocenyl-2-methylpropyl azide, 3654
* Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium), 3860
Nickelocene, 3281
Oxybis[bis(cyclopentadienyl)titanium], 3797
Pentamethylcyclopentadienyl-bis(thiolatothiatriazyl)rhodium, 3528
Poly(cyclopentadienyltitanium dichloride), 1837
* Tricyclopentadienyluranium tetrahydroaluminate, 3681
N,N,4-Trilithioaniline, 2173
Triphenylmethylpotassium, 3775
* Tris(2,4-pentanedionato)molybdenum(III), 3683
Tris(cyclopentadienyl)cerium, 3676
Tris(cyclopentadienyl)plutonium, 3677
Tris(cyclopentadienyl)uranium, 3678

ALKYLMETAL HALIDES

ALKYLMETALS

1-ARYL-1-VINYLLITHIUM DERIVATIVES

ARYLMETALS
GRIGNARD REAGENTS
HALO-ARYLMETALS
ORGANOLITHIUM REAGENTS

ORGANOSILYL PERCHLORATES R_3SiClO_4

Wannagat, U. *et al., Z. Anorg. Chem.*, 1950, **302**, 185—198
Several trialkyl- or triaryl-silyl perchlorates explode on heating, including:
Tri-4-methylphenylsilyl perchlorate, 3817
Triethylsilyl perchlorate, 2557
Trimethylsilyl perchlorate, 1298
Triphenylsilyl perchlorate, 3744
Tripropylsilyl perchlorate, 3212
See related NON-METAL PERCHLORATES

ORIGINS OF UNWANTED CHEMICAL REACTIONS

Rasmussen, B., *Unwanted Chemical Reactions in Chem. Processing Ind.*, Rept. M-2631, Roskilde (DK), Riso National Lab., 1987

A total of 190 published case histories of chemical processing accidents, selected from the MCA series, *Loss Prevention Bulletin, Loss Prevention* and elsewhere have been analysed to determine the underlying reasons for the unwanted chemical reactions. The most common reasons were:- incorrect storage or handling of materials, (24%); contamination or catalytic impurities, (20%); use of wrong chemicals, (19%); incorrect charging or processing conditions, (19%); insufficient agitation, (13%). Accidents in batch reactors were much more frequent than in continuous reactors.

In 55% of the cases,the accidents could have been foreseen by use of risk analysis, and in 35% of the cases by thermal stability testing. Different methods of stability testing were evaluated comparatively during the investigation of a runaway exothermic reaction which occurred during the preparation of a component mixture for a sealing composition in a 1200 l reactor: only DSC was effective in identifying the cause of the hazard.

A series of checklists is proposed to avoid such incidents in chemical processing operations, and an incompatibility chart for groups of reactive chemicals is given.

The methods used for the analysis of the case histories are detailed in a separate Appendix A, (Riso-278).

See Lead(IV) oxide: Carbon black, Chlorinated paraffin, Manganese(IV) oxide
See AGITATION INCIDENTS, CATALYTIC IMPURITY INCIDENTS, RUNAWAY REACTIONS
See also ACCELERATING RATE CALORIMETRY, REACTION SAFETY CALORIMETRY

2*H*-1,2,4-OXADIAZOLO[2,3-*a*]PYRIDINE-2-THIONES

Rousseau, D. *et al., Can. J. Chem.*, 1977, **55**, 3736—3739
The title compounds (R = H, 5-, 6-, 7-, or 8-methyl, or 5,7-dimethyl) explode at 121—137°C.
See other N—O COMPOUNDS

OXIDANTS

1. *Inorganic High Energy Oxidisers: Synthesis, Structure and Properties*, Lawless, E. W. and Smith, I. C., London, Arnold, 1968
2. *Hazard Classification of Oxidising Materials and Flammable Solids*, King P. V. *et al.*, Rept. PB-220084, Washington, US Dept. Transport, 1972
3. *NFPA 43A*, 1980; *NFPA 43B*, 1986; *NFPA 43C*, 1986, Quincy (Ma), National Fire Protection Association

Developments in inorganic fluorine oxidants, largely for rocketry, are covered [1]. A method of rating the potency of oxidants involves heating a carefully prepared and blended mixture of the solid oxidant with size-graded dried sawdust at 38.5°C/10 min to assess gross self-heating and ignition capability. Then a rectangular bed 2.5 cm deep x 5 x 17.5 cm is ignited at one end and the time taken for the combustion front to traverse 12.5 cm is taken as an inverse measure of oxidising power [2]. Three US fire codes cover the storage requirements for liquid or solid oxidants; for formulated organic peroxides; and for gaseous oxidants, respectively [3].

Members of this class of materials have been involved in the majority of the two-component reactive systems included in this Handbook, and the whole class is extremely large. Most oxidants have been treated collectively in the structurally based entries:
Other individually indexed compounds are:

Acetyl hypofluorite, 0748
* Ammonium hexanitrocerate, 3958
* Ammonium nitrate, 4517
Ammonium permanganate, 4513
Ammonium peroxodisulfate, 4571
Antimony pentachloride, 4178
Barium chlorite, 0204
Barium peroxide, 0216
* Bismuthic acid, 0228
Bromine, 0261
4-*tert*-Butyliodylbenzene, 3313
Caesium fluoroxysulfate, 4250
Calcium chromate, 3920
* Calcium hypochlorite, 3918
Calcium nitrate, 3929
Calcium permanganate, 3928
Calcium peroxide, 3932
Calcium peroxodisulfate, 3934
Calcium triperoxochromate, 3939
Chlorine, 4041
Chlorine dioxide, 4036
Chlorosulfuric acid, 3991
Chloryl perchlorate, 4098
Chromic acid, 4223
Chromium pentafluoride, 4220
Chromium trioxide, 4236
Chromyl acetate, 1490

* Chromyl chloride, 4048
* Chromyl fluorosulfate, 4219
* Chromyl perchlorate, 4049
Cobalt(II) nitrate, 4209
Di-*tert*-butyl chromate, 3061
Dichlorine oxide, 4089
Dilead(II)lead(IV) oxide, 4855
Dinitrogen oxide, 4739
Dinitrogen pentaoxide, 4743
Dinitrogen tetraoxide, 4720
Dinitrogen trioxide, 4741
Dioxonium hexamanganato(VII)manganate, 4548
Dioxygen difluoride, 4314
Dioxygenyl tetrafluoroborate, 0132
Dipyridinium dichromate, 3298
Fluorine, 4304
Fluorine fluorosulfate, 4318
Fluoroselenic acid, 4289
Graphite hexafluorogermanate, 3416
1,1,1,3,5,5,5-Heptanitropentane, 1848
Hydrogen peroxide, 4471
Iodic acid, 4418
Iodine, 4620
Iodine dioxide trifluoride, 4328
Iodine(V) oxide, 4622
Iodine(VII) oxide, 4623
Iridium hexafluoride, 4356
Lead chromate, 4237
Lead(II) nitrate, 4744
Lead(II) oxide, 4818
Lead(IV) oxide, 4828
Lithium chlorite, 4014
Magnesium nitrate, 4688
Magnesium nitrite, 4687
Magnesium permanganate, 4686
* Manganese fluoride trioxide, 4295
Manganese tetrafluoride, 4337
Manganese(IV) oxide, 4700
Manganese(VII) oxide, 4704
Mercury(II) bromate, 0269
Mercury(II) nitrate, 4598
Mercury(II) oxide, 4600
Monofluoroxonium hexafluoroarsenate, 0097
Neptunium hexafluoride, 4360
Nickel(II) nitrate, 3583
Nitric acid, 4430

Nitrogen dioxide, 4720
Nitrogen oxide, 4719
Nitrosyl chloride, 4017
Nitrosyl fluoride, 4296
Nitrosyl perchlorate, 4021
Nitrosyl tetrafluorochlorate, 3979
Nitrosylsulfuric acid, 4432
Nitrous acid, 4429
Nitryl chloride, 4019
Nitryl fluoride, 4297
Nitryl hypochlorite, 4020
Nitryl hypofluorite, 4298
Nitryl perchlorate, 4023
Osmium hexafluoride, 4364
Osmium(VIII) oxide, 4852
Oxygen difluoride, 4311
Oxygen (Gas), 4825
Oxygen (Liquid), 4826
Ozone, 4840
Palladium(II) oxide, 4819
Palladium(IV) oxide, 4829
Perchloric acid, 3992
Periodic acid, 4419
Permanganic acid, 4428
Peroxodisulfuric acid, 4476
Peroxodisulfuryl difluoride, 4322
Peroxomonosulfuric acid, 4475
Peroxytrifluoroacetic acid, 0662
Platinum hexafluoride, 4365
Platinum(IV) oxide, 4830
Plutonium hexafluoride, 4366
Potassium bromate, 0255
Potassium chlorate, 4011
Potassium dichromate, 4242
Potassium iodate, 4614
Potassium nitrate, 4645
Potassium nitrite, 4644
Potassium perchlorate, 4012
Potassium periodate, 4615
Potassium permanganate, 4642
Rhenium hexafluoride, 4367
Rubidium fluoroxysulfate, 4303
Ruthenium(VIII) oxide, 4856
Selenium dioxide, 4832
* Selenium dioxide, 4832
Silver permanganate, 0021

Sodium chlorate, 4033
Sodium chlorite, 4032
Sodium dichromate, 4244
Sodium iodate, 4619
Sodium nitrate, 4716
Sodium nitrite, 4715
Sodium perchlorate, 4034
Sodium permanganate, 4698
Sodium peroxide, 4797
Sodium peroxodisulfate, 4803
† Sulfur, 4891
Sulfur trioxide, 4843
Sulfuric acid, 4473
Tetrafluoroammonium hexafluoromanganate, 4378
Tetrafluoroammonium hexafluoronickelate, 4379
Tetrafluoroammonium hexafluoroxenate, 4380
Tetranitromethane, 0543
Titanium tetraperchlorate, 4164
1,1,1-Triacetoxy-1,2-benziodoxol-3-one, 3604
Trifluoromethyl hypofluorite, 0352
Trimethylsilyl chlorochromate, 1297
'Trioxygen difluoride', 4317
Uranium hexafluoride, 4369
* Vanadium trinitrate oxide, 4758
Vanadium(V) oxide, 4860
Vanadyl perchlorate, 4146
Xenon hexafluoride, 4371
Xenon tetrafluoride, 4347
Xenon tetrafluoride oxide, 4340
Xenon tetraoxide, 4857
Xenon trioxide, 4851
Xenon(II) pentafluoroorthoselenate, 4376
Xenon(II) pentafluoroorthotellurate, 4377
Zinc permanganate, 4705

ACETYLENIC PEROXIDES
ACYL HYPOHALITES
ALKYL HYDROPEROXIDES
ALKYL TRIALKYLLEAD PEROXIDES
AMINIUM IODATES AND PERIODATES
AMMINECHROMIUM PEROXOCOMPLEXES
BIS(FLUOROOXY)PERHALOALKANES
BLEACHING POWDER
CHLORITE SALTS
COMMERCIAL ORGANIC PEROXIDES
CRYSTALLINE HYDROGEN PEROXIDATES
CYCLIC PEROXIDES

DIACYL PEROXIDES
DIALKYL PEROXIDES
I,I-DI(BENZOYLPEROXY)ARYLIODINES
DIFLUOROAMINO COMPOUNDS
DIFLUOROAMINOPOLYNITROAROMATIC COMPOUNDS
DIFLUOROPERCHLORYL SALTS
DIOXETANES
DIOXYGENYL POLYFLUOROSALTS
FLUORINATED PEROXIDES AND SALTS
FLUORODINITRO COMPOUNDS
N-HALOGEN COMPOUNDS
HALOGEN OXIDES
HALOGENS
N-HALOIMIDES
HEXAFLUOROCHLORONIUM SALTS
HYDROXOOXODIPEROXOCHROMATE SALTS
HYPOHALITES
INORGANIC PEROXIDES
INTERHALOGENS
KETONE PEROXIDES
LIQUID AIR
METAL CHLORATES
METAL HALOGENATES
METAL HYPOCHLORITES
METAL NITRATES
METAL NITRITES
METAL OXIDES
METAL OXOHALOGENATES
METAL OXOMETALLATES
METAL OXONON-METALLATES
METAL PERCHLORATES
METAL PEROXIDES
METAL PEROXOMOLYBDATES
METAL POLYHALOHALOGENATES
MOLTEN SALT BATHS
NITROALKANES
NON-METAL PERCHLORATES
OXIDES OF NITROGEN
OXOHALOGEN ACIDS
OXYGEN ENRICHMENT
1-OXYPEROXY COMPOUNDS
OZONIDES
PERCHLORYL COMPOUNDS
PEROXOACID SALTS
PEROXOACIDS
PEROXYACIDS

PEROXYCARBONATE ESTERS
PEROXYESTERS
POLYNITROALKYL COMPOUNDS
POLYPEROXIDES
QUATERNARY OXIDANTS
TRINITROETHYL ORTHOESTERS
XENON COMPOUNDS

OXIDANTS AS HERBICIDES

Cook, W. H., *Can. J. Res.*, 1933, **8**, 509

The effect of humidity on combustibility of various mixtures of organic matter and sodium chlorate was studied. Addition of a proportion of hygroscopic material (calcium or magnesium chlorides) effectively reduces the hazard. Similar effects were found for sodium dichromate and barium chlorate.

See Sodium chlorate: Organic matter

OXIDATION INCIDENTS

Since the vast majority of the hazardous occurrences described in this volume involve oxidation reactions, it is not feasible to provide a comprehensive listing of the individual incidents. However, it may be noted that nitric acid and hydrogen peroxide are the two common oxidants most frequently involved in accidents.

See MICROWAVE OVEN HEATING, OXIDANTS, OXIDATION PROCESSES, SAMPLE DISSOLUTION

See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

OXIDATION PROCESSES

Kletz, T. A., *Plant/Oper. Progr.*, 1988, **7**, 226—230

Fire and explosion hazards of processes involving the oxidation of hydrocarbons are reviewed, including oxidation of cyclohexane to cyclohexanone/cyclohexanol, ethylene to ethylene oxide, of cumene to its hydroperoxide, and of *p*-xylene to terephthalic acid.

N-OXIDES $N \rightarrow O$

Baumgarten, H. E. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 3145

A procedure for preparing *N*-oxides is described which avoids formation of peroxyacetic acid. After prolonged treatment of the amine at 35—40°C with excess 30% hydrogen peroxide, excess of the latter is catalytically decomposed with platinum oxide.

Individually indexed compounds are:

2,2′-bipyridyl 1-oxide, 3252
2-Bromo-4-methylpyridine *N*-oxide, 2290
3-Bromopyridine *N*-oxide, 1822
* Decafluoro-2,5-diazahexane 2,5-dioxyl, 1368
2,3-Diazabicyclo[2.2.2]octa-2,5-diene *N*-oxide, 2367

5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3670
* Disodium 5,5′-azoxytetrazolide, 1015
Fulminic acid, 0380
4(1-Hydroxyethyl)pyridine *N*-oxide, 2816
1-Hydroxyimidazole *N*-oxide, 1131
3-Methyl-4-nitropyridine *N*-oxide, 2310
N-Methylmorpholine oxide, 1991
N-Methylpiperidine —N½-oxide, 2522
2-(*N*-Nitroamino)pyridine *N*-oxide, 1845
4-(*N*-Nitroamino)pyridine *N*-oxide, 1846
4-Nitropyridine *N*-oxide, 1827
2,2′-Oxybis(iminomethylfuran) mono-*N*-oxide, 3254
Pyridine *N*-oxide, 1843
Tribromamine oxide, 0290
Trimethylamine oxide, 1309
See also 3,3′-Azobis(6-amino-1,2,4,5-tetrazine
See FURAZAN N-OXIDES

OXIDES OF NITROGEN NO_n

The oxides of nitrogen collectively are oxidants with power increasing with oxygen content. Dinitrogen oxide will often support violent combustion, since its oxygen content (36.5%) approaches double that of atmospheric air. Nitrogen oxide and dinitrogen oxide are both endothermic and capable of detonation in the liquid state.
Individually indexed oxides are:
Dinitrogen oxide, 4739
Dinitrogen pentaoxide, 4743
Dinitrogen tetraoxide, 4720
Dinitrogen trioxide, 4741
Nitrogen dioxide, 4720
Nitrogen oxide, 4719

Glyptal resin
Anon., *ABCM Quart Safety Summ.*, 1937, **8**, 31
A new wooden fume cupboard was varnished with glyptal (glyceryl phthalate) resin. After a few weeks' use with 'nitrous fumes', the resin spontaneously and violently ignited. This was attributed to formation and decomposition of glyceryl trinitrate or similar compounds.

'Oxides of nitrogen' are thought to have been involved in several violent incidents.

In this latter context, hoowever, according to Henstock, W. H., *Plant/Oper. Progr.*, 1986, **5**, 232—237, no explosive products from hydrocarbon/oxides of nitrogen contact were found in a cryogenic hydrogen recovery unit processing petroleum refinery gases and cracked gases, and no such hazardous reactions seemed likely.
Nitrogen dioxide, : Alkenes, 4720
Nitrogen oxide, : Dienes, Oxygen, 4719

See Hydrogen (Gas), : Liquid nitrogen
Dinitrogen tetraoxide, : Unsaturated hydrocarbons, 4720
See other OXIDANTS

OXIME CARBAMATES C=NOCO.NHR

Pinnegar, M. A. *et al.*, UK Pat. 2 000 031, 1979

Oxime carbamates may explode on heating, after an induction period of very variable length, dependent upon temperature and impurities present.

See also OXIMES
See other INDUCTION PERIOD INCIDENTS, N—O COMPOUNDS

OXIMES RC=NOH

1. Horner, L. in *Autoxidation and Antioxidants*, Lundberg, W. O. (Ed.), Vol. 1, 184—186, 197—202, New York, Interscience, 1961
2. Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3
3. Cardillo, P. *et al., J. Loss Prev.*, 1993, **6**(2), 69

Several explosions or violent decompositions during distillation of aldoximes may be attributable to presence of peroxides arising from autoxidation. The peroxides may form on the —C=NOH system (both aldehydes and hydroxylamines peroxidise [1]) or perhaps arise from unreacted aldehyde. Attention has been drawn to an explosion hazard inherent to ketoximes and many of their derivatives (and not limited to them). The hazard is attributed to inadvertent occurrence of acidic conditions leading to highly exothermic Beckmann rearrangement reactions accompanied by potentially catastrophic gas evolution. Presence of acidic salts (iron(III) chloride, or the ketoxime hydrochloride) markedly lowers decomposition temperatures [2]. Dimethyl sulfate, ostensibly neutral and used to make methoximes, may not observably react at ambient temperature but also greatly facilitates runaway decomposition on warming.

A nickel catalysed aldoxime rearrangement, to an amide, went out of control after changing the solvent employed. This was found to be due to a slow start and consequent accumulation of unreacted substrate. Changing to a higher operating temperature restored control to the process [3].

Individually indexed compounds are:

† Acetaldehyde oxime, 0861
Acetone oxime, 1254
Azoformaldoxime, 0811
Benzaldehyde oxime, 2756
Bromoacetone oxime, 1197
Butane-2,3-dione dioxime, 1590
2,3-Butanedione monoxime, 1565
2-Butanone oxime, 1649
* 2-Butanone oxime hydrochloride, 1672
Butyraldehyde oxime, 1650
‘10-Carbon oxime’, 3356
Chloroacetaldehyde oxime, 0783
* 2-Chloro-*N*-hydroxyacetamidine, 0845
1,2,3-Cyclohexanetrione trioxime, 2394

1,3,5-Cyclohexanetrione trioxime, 2395
Cyclohexanone oxime, 2446
Cyclopentanone oxime, 1926
2,3-Epoxypropionaldehyde oxime, 1178
Ethyl 2-formylpropionate oxime, 2448
2-Ethylacryladehyde oxime, 1927
Furan-2-amidoxime, 1866
∗ Hydroxycopper(II) glyoximate, 0795
1-Hydroxyimidazole-2-carboxaldoxime 3-oxide, 1473
2-Isopropylacrylaldehyde oxime, 2447
∗ *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate, 3328
2-Methyl-2-[4-(2-methylpropyl)phenyl]oximinoethane, 3608
1-Nitro-1-oximinoethane, 0806
2-Nitroacetaldehyde oxime, 0805
∗ Nitrooximinomethane, 0408
3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid, 3125
2-Nitrosophenol (1,2-Benzoquinone monoxime), 2256
∗ 4-Nitrosophenol (1,4-Benzoquinone monoxime), 2257
4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2350
∗ Potassium 1-nitroethane-1-oximate, 0753
∗ Potassium cyclohexanehexone 1,3,5-trioximate, 2621
∗ Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1405
Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3499
∗ Sodium 3-methylisoxazolin-4,5-dione-4-oximate, 1415
∗ Sodium 3-phenylisoxazolin-4,5-dione-4-oximate, 3108
∗ Sodium 4-chloroacetophenone oximate, 2922
∗ Sodium tris(*O,O′*-1-oximatonaphthalene-1,2-dione)ferrate, 3865
Trichloroacetaldehyde oxime, 0694
∗ Trinitrosophloroglucinol, 2110

See KETOXIMINOSILANES

OXIRANES

See 1,2-EPOXIDES

OXOHALOGEN ACIDS $HOXO_n$

1. Bretherick, L., Comments, 1970
2. Alazard, J-P. *et al., Actual. Chim.*, 1995, (1), 49

The oxidising power of the group of oxohalogen acids increases directly with oxygen content, though the high stability of the perchlorate ion at ambient temperature must be taken into account. The corresponding ‘anhydrides’ (halogen oxides) are also powerful oxidants, several being explosively unstable [1]. A review has been published on the instability of, and consequent safety considerations for, oxygen derivatives of chlorine; oxides, acids and salts thereof, used in organic synthesis [2].

Individual compounds are:
Bromic acid, 0248
Chloric acid, 3990
Hypochlorous acid, 3989
Iodic acid, 4418
Orthoperiodic acid, 4537
Perchloric acid, 3992
Periodic acid, 4419
See also HALOGEN OXIDES

OXOSALTS OF NITROGENOUS BASES $N^+ EO_n^-$

1. Fogel'zang, A. G. *et al., Chem. Abs.*, 1971, **75**, 142412
2. Mikhailova, T. A. *et al., Chem. Abs.*, 1976, **85**, 201766

Burning rates of ammonium salts were investigated at various constant pressures. Ammonium permanganate burns faster than ammonium bromate, chlorate, dichromate, iodate, nitrite, perchlorate, periodate or triperchromate [1]. When submitting explosive nitrogenous bases or their salts to elemental nitrogen determination, it is advantageous to pre-treat the samples with phosphoric acid which allows the more stable pyro- and meta-phosphates (formed at 260° and 300°C, respectively) to be fully oxidised without explosion in the Dumas nitrogen procedure [2].

Many of the salts of nitrogenous bases (particularly of high nitrogen content) with oxoacids are unstable or explosive. There are separate group entries below and individually indexed compounds:

∗ Ammonium amidoselenate, 4552
Ammonium amidosulfate, 4551
Ammonium bromate, 0252
Ammonium chlorate, 3997
∗ Ammonium fluorochromate, 4218
∗ Ammonium nitrate, 4517
Ammonium permanganate, 4513
Ammonium tetrachromate(2—), 4247
Ammonium tetranitroplatinate(II), 4573
Ammonium trichromate(2—), 4246
Anilinium nitrate, 2372
2,2′-Azobis(2-amidiniopropane) peroxodisulfate, 3085
3-Azoniabicyclo[3.2.2]nonane nitrate, 3043
4-Chloro-1-methylimidazolium nitrate, 1449
Chloroformamidinium nitrate, 0466
1-(4-Chlorophenyl)biguanidinium hydrogen dichromate, 3000
Diaminoguanidinium nitrate, 0511
1,2-Diammonioethane nitrate, 0962
∗ 2-Diethylammonioethyl nitrate nitrate, 2566
Guanidinium nitrate, 0506
Hydrazinium chlorate, 4004
Hydrazinium dinitrate, 4556

Hydrazinium hydrogen selenate, 4553
Hydrazinium nitrate, 4544
Hydroxylaminium nitrate, 4519
2-Methoxyanilinium nitrate, 2825
1-Methyl-3-nitroguanidinium nitrate, 0943
Methylammonium chlorite, 0497
Methylammonium nitrate, 0503
Methylammonium nitrite, 0502
Methylhydrazinium nitrate, 0508
1-Phenylbiguanidinium hydrogen dichromate, 3014
Pyridinium nitrate, 1867
1,3,6,8-Tetraazoniatricyclo[6.2.1.$1^{3,6}$]dodecane tetranitrate, 3086
Tetraethylammonium periodate, 3084
Tetrafluoroammonium perbromate, 0242
* Tetrakis(hydroxymethyl)phosphonium nitrate, 1748
Tetramethylammonium chlorite, 1736
Tetramethylammonium pentaperoxodichromate, 3097
Triaminoguanidinium nitrate, 0514
Triethylammonium nitrate, 2575
Uronium nitrate, 0492
AMINIUM IODATES AND PERIODATES
AMINIUM PERCHLORATES
DIAZONIUM PERCHLORATES
DICHROMATE SALTS OF NITROGENOUS BASES
1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES
HYDROXYLAMINIUM SALTS
NITRITE SALTS OF NITROGENOUS BASES
PERCHLORATE SALTS OF NITROGENOUS BASES
POLY(AMINIUM) PERCHLORATES
See also CHLORITE SALTS

OXYGEN BALANCE

1. Kirk-Othmer, 1965, Vol. 8, 581
2. Slack, R., private comm., 1957

The oxygen balance of a compound is the difference between the oxygen content of the compound and that required fully to oxidise the carbon, hydrogen and other oxidisable elements present to carbon dioxide, water, etc. The concept is of particular importance in the design of explosive compounds or compositions, since the explosive power (energy release) is maximal at equivalence, or zero oxygen balance. If there is a deficiency of oxygen present, the balance is negative, while an excess of oxygen gives a positive balance, and such compounds can function as oxidants. The balance is usually expressed as a percentage. The nitrogen content of a compound is not considered as oxidisable, as it is usually liberated as the gaseous element in explosive decomposition [1].

While it is, then, possible to recognise highly explosive materials by consideration of their molecular formulae and oxygen balance (e.g. ethylene dinitrate, $C_2H_4N_2O_6$ is zero balanced, tetranitromethane, CN_4O_8 has +300% balance), the tendency to instability and high energy release becomes apparent well below the balance point. Trinitrotoluene has an oxygen balance of —64%. The empirical statement that the stability of any organic compound is doubtful when the oxygen content approaches that necessary to convert the other elements present to their lowest state of oxidation forms a useful guide [2] in the absence of more specific information. Some examples of oxygen balances may be found in the entries:

Bis(hydrazine)diperchloratochromium(III) perchlorate, 4122
Bis(triperchloratosilicon) oxide, 4184
5-Chloro-1,2,3-thiadiazole, 0651
Hexaamminechromium(III) perchlorate, 4123
Hexaamminecobalt(III) perchlorate, 4120
Mercury(II) oxalate, 0978
Pentaammineaquacobalt(III) chlorate, 4118
Tetraperchloratosilicon, 4163
Titanium tetraperchlorate, 4164
Trinitromethane, 0384

OXYGEN BOMB CALORIMETRY

Plewinsky, B. *et al., Thermochim. Acta*, 1985, **94**, 33—43

Safety aspects of the combustion of various materials in an amosphere of pure oxygen under the conditions prevailing in oxygen bomb calorimetry were investigated experimentally. The combustion of a stable substance (benzoic acid, used to calibrate bomb calorimeters) in oxygen gives a relatively slow combustion, with a low rate of pressure increase of 17 bar/s to a maximum of 64 bar in 2.3 s, for an initial oxygen pressure of 40 bar, and largely independent of the size of the sample. On the other hand, unstable (or explosive) solids may deflagrate or detonate, leading to very high rates of pressure increase and high maximum pressures, with values very dependent on sample size. Thus, under 40 bar oxygen pressure 0.5 g of picric acid gave values of 3.6 kbar/s to a maximum 98 bar, while 1.5 g gave 54 kbar/s to maximum 216 bar.

In the case of liquid non-explosive samples, three distinct situations can be discerned. First is where the gas phase composition lies outside the explosive range, and rates of pressure rise and maximum pressures attained are both modest and independent of sample size. Examples are benzene and hexamethyldisiloxane, which at 40 bar initial pressure of oxygen gave 36 bar/s to maximum 84 bar, and 63 bar/s to maximum 67 bar, respectively. Second is where the composition of the gas phase lies within the explosive range, as is observed with highly volatile liquids which give a single homogeneous phase, but the explosion pressure and rate of rise strongly depend on the sample size and the initial pressure of oxygen. For a fixed sample size of tetramethyldisiloxane, at an initial oxygen pressure of 10, 15, or 30 bar, rates of rise of 265, 60 and zero kbar/s to maxima of 113, 145 amd zero (no reaction), respectively, were measured. The third case is where the composition of the gas phase is outside the explosive range and the system is heterogeneous (relatively non-volatile liquids), and this has been observed using low initial oxygen pressures with tetramethyldisiloxane and pentamethyldisiloxane.

The former, at 15 bar initial oxygen pressure gave 1 kbar/s rise to 75 bar maximum, but at 20 bar a transition to 21 kbar/s to 121 bar maximum occurs, and at 30 bar to 90 kbar/s and 160 bar maximum is observed, the latter almost certainly involving heterogeneous detonation on the wick and shattering of the containing crucible. Pentamethyldisiloxane at 25 bar initial oxygen pressure shows a rate of rise of 60 bar/s to maximum 49 bar, but at 30 bar initial pressure the rate increases to 38 kbar/s to 205 bar maximum.

See Oxygen (Gas), : Sodium hydroxide, Tetramethyldisiloxane

See other CALORIMETRY

OXYGEN ENRICHMENT

1. *Oxygen Enrichment of Confined Areas*, Information Sheet, Inst. of Welding, 1966
2. Wilk, I. J., *J. Chem. Educ.*, 1968, **45**, A547—551
3. Johnson, J. E. *et al., NRL Rept. 6470*, Washington, Nav. Res. Lab., 1966
4. Woods, F. J. *et al., NRL Rept. 6606*, Washington, Nav. Res. Lab., 1967
5. Denison, D. M. *et al., Nature*, 1968, **218**, 1111—1113
6. Jones, D. A., *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 1, I13—I22, Rugby, IChE, 1983
7. *NFPA 53M*, Quincy (Na), Natl. Fire Prot. Assocn., 1985
8. ASTM, *STP 1319 (Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres)*, 1997
9. Fehlings M. *et al., Chem Abs*, 1999, 130, 300864t

With the widening availability and industrial use of oxygen, accidents caused by atmospheric enrichment have increased. Most materials, especially clothing, burn fiercely in an atmosphere containing more than the usual 21 vol% of oxygen. In presence of petroleum products, fire and explosion can be spontaneous. Equipment which may emit or leak oxygen should be used sparingly, and never stored, in confined spaces [1]. Fourteen case histories of accidents caused by oxygen enrichment of the atmosphere are discussed and safety precautions detailed [2]. The flammability of textiles and other solids was studied under the unusual conditions which occur in deep diving operations. The greatest effect on ease of ignition and linear burning rate was caused by oxygen enrichment; increase in pressure had a similar effect [3].

Ignition and flame spread of fabrics and paper were measured at pressures from 21 bar down to the limiting pressure for ignition to occur. Increase in oxygen concentration above 21% in mixtures with nitrogen caused rapid decrease of minimum pressure for ignition. In general, but not invariably, materials ignite less readily but burn faster in helium mixtures than in nitrogen mixtures. The nature of the material has a marked influence on the effect of variables on the rate of burning. At oxygen concentrations of 41% all materials examined would burn except for glass and polytetrafluoroethylene, which resisted ignition attempts in pure oxygen. Flame retardants become ineffective on cotton in atmospheres containing above 32% oxygen [4]. A brief summary of known hazards and information in this general area was published [5]. Replacement of the nitrogen in air by a gaseous alkane considerably increases the oxygen index for explosion of propene during oxidation processes. The alkane is not consumed. This may well prove true for other alkenes capable of allylic oxidation [9]. A method of assessing off-site hazards in the vicinity of bulk liquid oxygen storage installations is presented [6]. The US Fire Protection Association manual covers materials and system design to reduce fire hazards in enriched atmospheres, and includes detail on fire experiences in such systems [7]. The American Society for Testing and Materials has produced an even more comprehensive work [8].

See Oxygen (Gas)

See Propene: air or oxygen

OXYGEN FLUORIDES O_2F, FOF, FOOF, O_2FOF, $(O_2F)_2$

Streng, A. G., *Chem. Rev.*, 1963, **63**, 607

In the series oxygen difluoride, dioxygen difluoride, trioxygen difluoride and tetraoxygen difluoride, as the oxygen content increases, the stability decreases and the oxidising power increases, tetraoxygen difluoride, even at —200°C, being one of the most potent oxidants known. Applications to both chemical reaction and rocket propulsion systems are covered in some detail.

Individual compounds are:

Dioxygen difluoride, 4314
Hexaoxygen difluoride, 4321
Oxygen difluoride, 4311
'Trioxygen difluoride', 4317

See other HALOGEN OXIDES

OXYGEN INDEX

1. *Oxygen Index Test*, ASTM D2863, 1970
2. Isaacs, J. S., *J. Fire Flamm.*, 1970, **1**, 36—47
3. Kamp, A. C. F. *et al., Proc. 1st Euro. Symp. Therm. Anal.*, 1976, 440—443
4. Redfern, J. P., *Intern. Lab.*, 1979, **9**, 57
5. Kishore, K. *et al., J. Haz. Mat.*, 1980, **3**, 349—356

The flammability properties of volatile materials are readily gauged from the values of the figures for flash point and limits of flammability in air. For involatile flammable materials, a range of empirical tests provides a measure of flammability properties under various circumstances. One of the tests, originally developed to measure the minimum concentration of oxygen in which a sample of a plastics material will continue to burn candle-like, is simple, accurate and reproducible [1]. Results are expressed as an Oxygen Index (O. I.), which is the minimum proportion of oxygen in a mixture with nitrogen to just sustain combustion of a sample of standard size in a chimney-like apparatus. The method has been applied to textile materials [2], and may well be applicable to a much wider range of materials. Determination of the Oxygen Index over a wide temperature range gives a better understanding of flammability parameters, and the Temperature Index (T. I., the temperature at which O. I. is 20.8) will rank flammability of materials. The O. I. at ambient temperature indicates potential hazard at the primary ignition stage, while the T. I. and the O. I.—temperature relation is related to practical fire situations [3]. The mathematical relationships between O. I. and various fire parameters have been reviewed [4]. A new (dimensionless) parameter for flammability of materials, the Flammability Index, is defined in terms of specific heat, flash or autoignition temperature and heat of combustion. It correlates well with the Oxygen Index [5].

1-OXYPEROXY COMPOUNDS O—C—OO—

Swern, 1970,, Vol. 1, 29, 33

This group of compounds includes those monomers with one or more carbon atoms carrying a hydroperoxy or peroxy group, and also singly bonded to an oxygen atom present as hydroxyl, ether or cyclic ether functions. While the group of compounds is, in general, moderately stable, the lower 1-hydroxy and 1,1′-dihydroxy-alkyl peroxides or hydroperoxides are explosive. Individually indexed compounds are:

1-Acetoxy-1-hydroperoxy-6-cyclodecanone, 3662
* 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide, 3541
Bis(1-hydroperoxycyclohexyl) peroxide, 3550
Bis(1-hydroxycyclohexyl) peroxide, 3547
Bis(hydroxymethyl) peroxide, 0924
1-Hydroperoxy-1′-hydroxydicyclohexyl peroxide, 3549
* 1-Hydroxy-3-butyl hydroperoxide, 1700
Hydroxymethyl hydroperoxide, 0485
Hydroxymethyl methyl peroxide, 0922
* 2-Methoxyprop-2-yl hydroperoxide, 1701

OZONIDES

1. Rieche, *Angew. Chem.*, 1958, **70**, 251
2. Swern, 1970, Vol. 1, 39
3. Bailey, P. S., *Chem. Rev.*, 1958, **58**, 928
4. Greenwood, F. L. *et al., J. Org. Chem.*, 1967, **32**, 3373
5. Rieche, A. *et al., Ann.*, 1942, **553**, 187, 224

The preparation, properties and uses of ozonides have been reviewed comprehensively [1]. Many pure ozonides (trioxolanes) are generally stable to storage; some may be distilled under reduced pressure. The presence of other peroxidic impurities is thought to cause the violently explosive decomposition often observed in this group [2]. Use of ozone is not essential for their formation, as they are also produced by dehydration of α,α′-dihydroxy peroxides [3]. A very few isomeric linear trioxides (ROOOR) are known, they are also explosively unstable. Inorganic ozonides, mostly salts of the radical O_3^- anion, are also hazardous.

Polymeric alkene ozonides are shock-sensitive; that of *trans*-2-butene exploded when exposed to friction in a ground glass joint. The use of GLC to analyse crude ozonisation products is questionable because of the heat-sensitivity of some constituents [4]. Ozonides are decomposed, sometimes explosively, by finely divided palladium, platinum or silver, or by iron(II) salts [5]. Individually indexed compounds are:

Benzene triozonide, 2336
trans-2-Butene ozonide, 1618
† 1,1-Dichloroethylene, : Ozone, 0691
1,1-Difluoroethylene ozonide, 0699
∗ 2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide, 2381
2,6-Dimethyl-2,5-heptadien-4-one diozonide, 3170
1,2-Dimethylcyclopentene ozonide, 2841
2,5-Diphenyl-3,4-benzofuran-2,5-endoperoxide, 3792
Ethylene ozonide, 0832
Fluoroethylene ozonide, 0749
trans-2-Hexene ozonide, 2507
4-Hydroxy-4-methyl-1,6-heptadiene diozonide, 3031
Isoprene diozonide, 1914
Maleic anhydride ozonide, 1402
3-Methyl-1,2,4-trioxolane, 1231
† 2-Methyl-1,3-butadiene: Ozone, 1887
trans-2-Pentene ozonide, 1976
Pyrocatecholato(2-)(quinolin-8-olato-*N,O*)-trioxygenido(2-)phosphorus, 3671
3,3,5-Trifluoro-1,2,4-trioxolane, 0663
Vinyl acetate ozonide, 1538
JOJOBA WAX: OZONE

PACKAGING INCIDENTS

Tobias, B. I., *Chem. Eng. News,* 1991, **69**(10), 2

A 500 ml bottle of peracetic acid (ethaneperoxoic acid), provided with a vented cap, was received packed within a tin padded with what appeared to be paper. The metal was distinctly hot to the touch on opening. Peroxyacetic acid is capable of runaway decomposition from 65°C. The heat is thought to have resulted from seepage through the vent, the bottle having been on its side, followed by reaction with the paper. The importance of inert packing materials is emphasised. Other packaging incidents are:

Acetyl chloride: Water, 0731
Benzenesulfinyl chloride, 2227
Benzenesulfonyl chloride, 2228
Borane—Tetrahydrofuran, 0138
Calcium oxide: Water (reference 5), 3931
Diethyl dicarbonate, 2438
Ethyl oxalyl chloride, 1451
Formic acid, 0417
Nitric acid: Polyalkenes, 4430
Nitric acid: Wood, 4430
Peroxyacetic acid, 0833
Potassium (reference 3), 4640
Pyruvic acid, 1147

Sodium sulfide: Glass, 4805
Trichloromethyl carbonate, 1039
See also INSULATION, PAPER TOWELS

PAINT TAILINGS

See 9,12,15-Octadecatrienoic acid: Cobalt naphthenate

PAPER TOWELS

Unpublished observations, 1970

The increasing use of disposable paper towels and wipes in chemical laboratories accentuates the potential fire hazards arising from the disposal of solid oxidising agents or reactive residues into a bin containing such towels or wipes. The partially wet paper, necessarily of high surface area and absorbency, presents favourable conditions for a fire to be initiated and spread. Separate bins for paper towels etc., and chemical residues seem advisable.

See Perchloric acid: Paper, Silver compounds
See Zinc: Sodium hydroxide (reference 3)
SODA-LIME
See also ALDEHYDES, INSULATION, PACKAGING INCIDENTS

PEAT

1. Sansonov, L. N. *et al., Chem. Abs.*, 1988, **109**, 173306
2. Kashinskaya, I. Ya. *et al., Chem. Abs.*, 1989, **110**, 26472

Stockpiles of milled peat are prevented from self heating and ignition by sprayed application of bitumen emulsion to form a 2—2.5 mm protective permeable film [1]. The mechanism of self heating and ignition first involves aerobic microbiological processes, then chemical transformation of iron-containing minerals in the peat into pyrophoric iron compounds which later ignite the peat mound [2].

DUST EXPLOSION INCIDENTS (reference 21)
See also PYROPHORIC IRON—SULFUR COMPOUNDS

PENTAAZADIENES ArN=NNRN=NAr

See Bis[1,5-bis(4-methylphenyl)-1,3-pentazadienato-N3,N5]-(T-4) cobalt
See TRIAZENES (reference 3)
See other HIGH-NITROGEN COMPOUNDS

N—PENTAFLUOROSULFUR COMPOUNDS R_2NSF_5

1. Sitzmann, E., *Chem. Abs.,* 1992, **116**, 132303z
2. De Yong, L. V. *et al., Chem. Abs.,* 1993, **119**, 142309g

A series of carbonimidate esters bearing a pentafluorosulfur group on the nitrogen are described as explosives. The SF_5 is unlikely to be ornamental although most of the alkoxy groups involved also carry nitro groups [1]. However, another study of explosives which bore a pentafluorothio group, probably on carbon, suggested it was equivalent to an hydrogen [2].

PENTAZOLES

Ugi, I., *Comprehensive Heterocyclic Chemistry*, (Ed. Katritzky, A. R.), Vol. 5, 843, Oxford, Pergamon, 1984

Although pentazoles have often been claimed, the only authentic isolated examples now accepted are aryl pentazoles. These are unstable, explosively so above an initial decomposition temperature, —5°C for phenylpentazole, 50°C for the 4-dimethylamino analogue. The structure is stabilised by electron donors [1]. Pentazole itself has lately been detected as an intermediate in solution. Pentazoles decompose to nitrogen and azides, which latter explosive materials were presumably previously claimed as pentazoles.

PERCHLORATE-DOPED CONDUCTING POLYMERS

1. Eisenbaumer, R. L.. *et al., Chem. & Eng. News*, 1985, **63**(22), 4
2. Young, X.-Z. *et al., J. Polymer Sci. (Polymer Chem. Edn.)*, 1985, **23**, 859
3. Varyu, M. E. *et al., Chem. & Eng. News*, 1985, **63**(24), 4
4. Österholm, J.-E. *et al., Chem. & Eng. News*, 1986, **64**(6), 2
5. Druy, M. A., *Chem. Eng. News*, 1986, **64**(12), 2
6. Julia, L. *et al., Chem. & Ind.*, 1989, 78—79
7. Editor’s comments

A piece of poly(acetylene) film doped with perchlorate detonated spontaneously inside an argon-filled dry box. Doping had been effected by contacting the film with a solution of iron(III) perchlorate in toluene—nitromethane, followed by washing and high-vacuum drying. Samples of the doped film had previously been tested and showed no signs of instability under impact, physical stress, or on flame contact. The explosion occurred 2 weeks later when further samples were being taken [1]. A sample of similar material undergoing thermogravimetric analysis had exploded at 160°C [2]. Use of electrochemical (rather than chemical) doping methods is preferred as more controlable, with determination of perchlorate content (as chloride) by oxygen flask combustion analysis. Limitation of analytical sample size to 10 mg and other precautions are recommended [3]. Perchlorate-doped poly(thiophene) film (up to 25—30 mol % of perchlorate in the matrix) has also been prepared and found stable under ambient conditions. However it is extremely unstable at temperatures above 100°C (possibly explosive), and samples of film intensively desiccated over phosphorus pentaoxide have exploded on handling with tweezers. Great care is necessary in handling such materials [4]. Perchlorate-doped poly(pyrrole) and poly(thiophene) film in a dry atmosphere tend to explode when handled with tweezers, though such films were stable to heating at above 100°C. Trifluoromethanesulfonate and *p*-toluenesulfonate are more suitable doping counterions than perchlorate [5]. The use of thallium(III) trifluoroacetate in trifluoroacetic acid as combined oxidant and dopant appears to give stable radical ion salts of poly(thiophene) [6].

Some conducting polymers with a conjugated polyvinyl structure, such as polyacetylene and poly(phenylacetylene), seem likely to be energetic enough, and reactive enough, to give trouble undoped, if they actually have the supposed structure [7].
See Ethylene, Butadiene, Styrene
See related NON-METAL PERCHLORATES

PERCHLORATES —$OClO_3$

1. Schumacher, 1960
2. Burton, H. *et al., Analyst*, 1955, **80**, 4
3. Long J. R., *Chem. Eng. News*, 2000, **78**(22), 8
4. Long, J. R., *Chem. Health & Safety*, 2002, 9(3), 12

All perchlorates have some potential for hazard when in contact with other mutually reactive materials, while many are intrinsically hazardous, owing to the high oxygen content.

Existing knowledge on perchloric acid and its salts was reviewed extensively in 1960 in a monograph including the chapters: Perchloric Acid; Alkali Metal, Ammonium and Alkaline Earth Perchlorates; Miscellaneous Perchlorates; Manufacture of Perchloric Acid and Perchlorates; Analytical Chemistry of Perchlorates; Perchlorates in Explosives and Propellants; Miscellaneous Uses of Perchlorates; Safety Considerations in Handling Perchlorates [1]. There is a shorter earlier review, with a detailed treatment of the potentially catastrophic acetic anhydride—acetic acid—perchloric acid system. The violently explosive properties of methyl, ethyl and lower alkyl perchlorate esters, and the likelihood of their formation in alcohol—perchloric acid systems, are stressed. The instability of diazonium perchlorates, some when damp, is discussed [2]. More recent recommendations on safe handling are found in [4]. It is recommended that any new perchlorate be tested for shock and thermal hazard before moving beyond the milligram scale, especially if it is dry or unhydrated [3].

The class has been divided into the separately treated groups:

ALKYL PERCHLORATES
AMINIUM PERCHLORATES
AMMINEMETAL OXOSALTS
DIAZONIUM PERCHLORATES
METAL PERCHLORATES
NON-METAL PERCHLORATES
PERCHLORATE SALTS OF NITROGENOUS BASES

Glycol, Polymer
MCA Case History No. 464
A mixture of an inorganic perchlorate salt, a glycol and a polymer exploded violently after heating at 265—270°C. It was thought that the glycol may have been oxidised, but formation of the glycol perchlorate ester(s) seems a likely alternative cause.

Organic matter
Schumacher, 1960, 188

Mixtures of perchlorate salts with finely divided or fibrous organic materials are likely to be explosive. Porous or fibrous materials exposed to aqueous solutions and then dried are rendered explosively flammable and are easily ignited.

Perchlorate complexes with organic ligands and organometallic perchlorates represent exceptionally intimate mixture with organic matter. Heating such materials is never advisable, many are also shock and friction sensitive.

Reducants

1. Mellor, 1941, Vol. 2, 387; Vol. 3, 651
2. Schumacher, 1960, 188

Perchlorate salts react explosively when rubbed in a mortar with calcium hydride or with sulfur and charcoal, when melted with reducants, or on contact with glowing charcoal [1]. Mixtures with finely divided aluminium, magnesium, zinc or other metals are explosives [2].

See other REDOX REACTIONS

PERCHLORATE SALTS OF NITROGENOUS BASES $N^+ ClO_4^-$

Kozak, G. D. *et al., Chem. Abs.*, 1981, **94**, 86609

In a study of detonation of aqueous solutions of perchlorate salts of hydroxylamine, urea, methylamine and diaminoethane (mono- or di-salts), the former could be detonated in 20—25% solution at 407—587°C.

Many other perchlorate salts of nitrogenous bases have been involved in explosive incidents, individually indexed compounds being:

2-Aminoethylammonium perchlorate, 0954
Ammonium perchlorate, 3998
Anilinium perchlorate, 2360
2-Aza-1,3-dioxolanium perchlorate, 0894
* 2-Azatricyclo[2.2.1.0^{2,6}]hept-7-yl perchlorate, 2361
* 1,4-Bis(2-chloroethyl)-1,4-bis(azonia)bicyclo[2.2.1]heptane periodate, 3186
1,2-Bis(ethylammonio)ethane perchlorate, 2585
Chloroformamidinium perchlorate, 0468
1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate, 3334
1,3-Dimethyl-2,1-benzisoxazolium perchlorate, 3142
Dimethylammonium perchlorate, 0946
1,1-Dimethyldiazenium perchlorate, 0934
2,2-Dimethyltriazanium perchlorate, 0959
2,4-Dinitrophenylhydrazinium perchlorate, 2344
N,N-Diphenyl-3-phenylpropenylidenimmonium perchlorate, 3814
2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate, 3402
1,2-Ethylenebis(ammonium) perchlorate, 0960
Guanidinium perchlorate, 0499
Hydrazinium diperchlorate, 4062
Hydrazinium perchlorate, 4005
2-Hydroxyethylaminium perchlorate, 0947
Hydroxylaminium perchlorate, 3999
1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate, 3168

1-Methyl-3-nitroguanidinium perchlorate, 0935
Methylammonium perchlorate, 0498
Morpholinium perchlorate, 1674
4-Nitroanilinium perchlorate, 2343
Perchloric acid, : Nitrogenous epoxides, 3992
* Phosphonium perchlorate, 4000
Poly(dimercuryimmonium perchlorate), 4006
Pyridinium perchlorate, 1857
Tetraethylammonium perchlorate, 3082
Tetrafluoroammonium perchlorate, 3980
N,N,N′,N′-Tetramethylformamidinium perchlorate, 2020
Tri(4-tolyl)ammonium perchlorate, 3818
Triaminoguanidinium perchlorate, 0512
Trimethylammonium perchlorate, 1318
Trimethylhydroxylammonium perchlorate, 1319
Uronium perchlorate, 0489

PERCHLORYLAMIDE SALTS $M^+ (O_3ClNH)^-$

1. *Perchloryl Fluoride*, Booklet DC-1819, Philadelphia, Pennsalt Chem. Corp., 1957
2. Hennrichs, W. *et al., Z. Anorg. Chem.*, 1983, **506**, 205

Ammonium perchlorylamide and the corresponding silver and barium salts are shock-sensitive when dry and may detonate. Extreme care is required when handling such salts [1]. Some *N*-benzylperchlorylamide derivatives are also unstable, and the barium, silver and mercury salts explode on impact, and the two latter on heating to 105 and 120°C, respectively [2].

Individually indexed compounds are:
Ammonium perchlorylamide, 4003
Barium *N*-perchlorylbenzylamide, 3642
Barium perchlorylamide, 0203
Mercury(II) *N*-perchlorylbenzylamide, 3644
Monopotassium perchlorylamide, 3988
Potassium perchlorylamide, 4013
Silver *N*-perchlorylbenzylamide, 2730
Silver perchlorylamide, 0028
See other N-METAL DERIVATIVES, PERCHLORYL COMPOUNDS

PERCHLORYL COMPOUNDS $RNHClO_3$, $ArClO_3$

1. *Friedel-Crafts and Related Reactions*, Olah, G. A. (Ed.), Vol. 3.2, 1507—1516, New York, Interscience, 1964
2. Baum, K. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 3233—3237
3. Beard, C. D. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 3237—3239

The need for great care to avoid the possibility of detonation of perchloryl compounds by exposure to shock, overheating or sparks is stressed. The compounds are generally more sensitive to impact than mercury fulminate and are of comparable sensitivity to lead azide [1]. A range of highly explosive alkyl perchlorates [2] and perchlorylamines [3] have been prepared by interaction of dichlorine heptaoxide with alcohols or amines in carbon tetrachloride solution. The solutions of the products were not sensitive to mechanical shock and could be used directly for further reactions. Adequate warning of the explosion hazards involved in isolating perchloryl compounds is given.

Individually indexed compounds are:
2,6-Dinitro-4-perchlorylphenol, 2094
2,6-Diperchloryl-4,4′-diphenoquinone, 3438
3-Nitroperchlorylbenzene, 2136
Perchloryl fluoride, 3968
Perchlorylbenzene, 2229
N-Perchlorylpiperidine, 1943
See also PERCHLORYLAMIDE SALTS

PERFLUOROSILANES Si_mF_n

Bailar, 1973, Vol. 1, 1385

The compounds in this group (Si_2F_6 to Si_4F_{10} are mentioned later) are said to ignite in air and react violently with water.

See other HALOSILANES

PEROXIDATION INCIDENTS

Many incidents involving explosions have been attributed, not always correctly, to peroxide formation and violent decomposition. Individually indexed incidents are:
2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one, 2803
Aluminium dichloride hydride diethyl etherate, : Dibenzyl ether, 0061
† 1,3-Butadiene, 1476
† Diallyl ether, 2425
† Diisopropyl ether, 2537
Lithium tetrahydroaluminate, : Tetrahydrofuran, 0075
Peroxyacetic acid, : Ether solvents, 0833
† 2-Propen-1-ol, : Sulfuric acid MRH 1.42/53, 1219
Sulfinyl chloride, : Diisopropyl malonate, 4090
See PEROXIDES IN SOLVENTS, PEROXIDISABLE COMPOUNDS
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

PEROXIDES —OO—

This class name covers one of the largest classes of hazardous compounds, with 3 main divisions: these groups are further subdivided for convenience.

INORGANIC PEROXIDES
ORGANIC PEROXIDES
ORGANOMETALLIC PEROXIDES

PEROXIDES IN SOLVENTS

1. Author's comments, 1984
2. Burfield, D. R., *J. Org. Chem.*, 1982, **47**, 3821—3824

Many laboratory accidents have been ascribed to presence of peroxides in solvents, usually, but not exclusively ethers. Storage of the solvents for over-long periods, often under poor conditions, is a common feature of the incidents. When peroxides are removed from solvents by chromatographic adsorption on alumina columns, the concentrated band of strongly adsorbed peroxides at the top of the column may become hazardous if the solvent evaporates [1]. The use of self-indicating molecular sieve under nitrogen is described as an effective method of de-peroxidising THF, diethyl and dipropyl ethers, suitable also for bulk-scale operations [2].

2-Butanol
2-Butanone
Diethyl ether
Diisopropyl ether
1,4-Dioxane
Hydrogen peroxide: Acetone
4-Methyl-2-pentanone
PEROXIDE TEST STRIPS
PEROXIDISABLE COMPOUNDS
Peroxomonosulfuric acid: Acetone
2-Propanol
Tetrahydrofuran
See ETHERS

PEROXIDE TEST STRIPS

See 1-Allyloxy-2,3-epoxypropane
See also PEROXIDES IN SOLVENTS

PEROXIDISABLE COMPOUNDS

1. Jackson, H. L. *et al., J. Chem. Educ.*, 1970, **47**, A175
2. Brandsma, 1971, 13
3. *MCA Case History No. 1693*
4. *Recognition and Handling of Peroxidisable Compounds*, Data sheet 1-655, Chicago, National Safety Council, 1982
5. Shanley, E. S., *Chem. Eng. News*, 1979, **57**(21), 43
6. Mirafzal, G. A. *et al., J. Chem. Educ.*, 1988, **65**(9), A226—229
7. Bretherick, L., private comm. to Dr Mirafzal, 1988; *J. Chem. Educ.*, 1990, **67**(9), A230
8. Kelly, R. J., *Chem. Health & Safety*, 1996, **3**(5), 28
9. Hobson, L. A. et al., *Chem. Eng. News*, 2000, **78**(51), 2

An account of a Du Pont safety study of the control of peroxidisable compounds covers examples of peroxidisable structures, handling procedures, distillation of peroxidisable compounds, and detection and elimination of peroxides [1]. Essential organic structural features for a peroxidisable hydrogen atom are recognised as those listed below. While the two structural types at the end of that list readily peroxidise, in some cases the products are readily degradable and do not accumulate to a hazardous level. A notable exception is acetaldehyde which is converted to peroxyacetic acid. Inorganic compounds which readily peroxidise are listed as potassium (which gives the superoxide) and higher alkali metals, alkali metal alkoxides and amides, and organometallic compounds.

Three lists of specific compounds or compound types indicate different types of potential hazard, and appropriate storage, handling and disposal procedures are detailed for each.

List A, giving examples of compounds which form explosive peroxides while in storage, include diisopropyl ether, divinylacetylene, vinylidene chloride, potassium and sodium amide. Review of stocks and testing for peroxide content by given tested procedures at 3-monthly intervals is recommended, together with safe disposal of any peroxidic samples.

List B, giving examples of liquids where a degree of concentration is necessary before hazardous levels of peroxides will develop, includes several common solvents containing one ether function (diethyl ether, ethyl vinyl ether, tetrahydrofuran), or two ether functions (*p*-dioxane, 1,1-diethoxyethane, the dimethyl ethers of ethylene glycol or ‘diethylene glycol’), the secondary alcohols 2-propanol and 2-butanol, as well as the susceptible hydrocarbons propyne, butadiyne, dicyclopentadiene, cyclohexene and tetra- and deca-hydronaphthalenes. Checking stocks at 12 monthly intervals, with peroxidic samples being discarded or repurified, is recommended here [1].

A simple method of effectively preventing accumulation of dangerously high concentrations of peroxidic species in distillation residues is that detailed in an outstanding practical textbook of preparative acetylene chemistry [2]. The material to be distilled is mixed with an equal volume of non-volatile mineral oil. This remains after distillation as an inert diluent for polymeric peroxidic materials.

List C contains peroxidisable monomers, where the presence of peroxide may initiate exothermic polymerisation of the bulk of material. Precautions and procedures for storage and use of monomers with or without the presence of inhibitors are discussed in detail. Examples cited are acrylic acid, acrylonitrile, butadiene, 2-chlorobutadiene, chlorotrifluoroethylene, methyl methacrylate, styrene, tetrafluoroethylene, vinyl acetate, vinylacetylene, vinyl chloride, vinylidene chloride and vinylpyridine [1].

In general terms, the presence of two or more of the structural features indicated above in the same compound will tend to increase the risk. The selection of compound groups and of individually indexed compounds below includes compounds known to have been involved or those with a multiplicity of such structural features which would be expected to be especially susceptible to peroxide formation. A more recent and thorough review of peroxidation risks gives a critical assessment of test methods for peroxides [8].

Subsequent to incidents involving peroxidation of stored bottles of vinylidene chloride, a labelling procedure and list of peroxidisable compounds was prepared [3]. Of the 108 compounds listed, 35 are noted as forming peroxides with ease, and these need particular care in storage and use. A revised data sheet is now available [4], and peroxide-containing residues may often be rendered innocuous by pouring into an excess of sodium carbonate solution [5].

The argument in an addendum to reference 1 above which claims that primary alcohols should also be classed as peroxidisable [6] is flawed. Among the primary alcohols listed as peroxide formers, the structures of those which formed significant levels of peroxide in storage all possessed tertiary H atoms susceptible to autoxidation by virtue of their position on the branched carbon skeletons of the alcohols, as well as the (insusceptible) primary hydroxyl group. While it is true that secondary alcohols should certainly be added to List B above, it is not necessary for primary alcohols as such, unless the structure is branched, when there may be susceptible hydrogen(s) present to warrant caution. It is the nature of the carbon skeleton, rather than presence of the hydroxyl group, which is the more important factor [7]. Some evidence for primary alcohol peroxidation may have been shown by the discovery of low levels of peroxide, apparently as peroxyacetic acid, in ethyl acetate. This was attributed to autoxidation of ethanol (the usual impurity) to acetaldehyde, which readily picks up oxygen to give peracetic acid. There is no suggestion that the reported levels were hazardous [9]

BOND GROUPINGS	*EXAMPLES (not exhaustive)*
$R_2C\mathbf{H}$—	Isopropyl compounds, decahydronaphthalenes
C=C—C**H**—	Allyl compounds
C=C**H**X	Haloalkenes
C=C**H**—	Other vinyl compounds – ethers, esters etc.
C=C**H**—CH=C	Dienes
C=C**H**—C≡C	Vinylacetylenes
C—C**H**Ar	Cumenes, tetrahydronaphthalenes, styrenes
HC=O	Aldehydes
O=C—N—$C\mathbf{H}R_2$	*N*-alkyl-amides, -ureas or -lactams

and individually indexed compounds:

† Acetaldehyde, 0824
† Acrylaldehyde, 1142
† Allyl ethyl ether, 1949
1-Allyloxy-2,3-epoxypropane, 2428
† Bis(2-ethoxyethyl) ether, 3071
Bis-(2-methoxyethyl) ether, 2544
† 1,3-Butadiene, 1476
† 1,3-Butadiyne, 1381
† 2-Butanol, 1689
† Buten-3-yne, 1419
† Butyl ethyl ether, 2535
† Butyl vinyl ether, 2478
† 2-Chloro-1,3-butadiene, 1447
† 2-Chloroethyl vinyl ether, 1552
† Chloroethylene, 0726
Cinnamaldehyde, 3128
† Crotonaldehyde, 1513

† Cyclopropyl methyl ether, 1603
Di(2-propynyl) ether, 2320
† Diallyl ether, 2425
Dibenzyl ether, 3648
† Dibutyl ether, 3066
† 1,1-Dichloroethylene, 0691
† 1,1-Diethoxyethane, 2540
† 1,2-Diethoxyethane, 2541
† 3,3-Diethoxypropene, 2854
† Diethyl ether, 1691
Diethylketene, 2424
† 2,3-Dihydrofuran, 1514
† Diisopropyl ether, 2537
† 1,2-Dimethoxyethane, 1695
† 1,1-Dimethoxyethane, 1694
† Dimethoxymethane, 1277
† 3,3-Dimethoxypropene, 1962
† 1,3-Dioxane, 1611
† 1,4-Dioxane, 1612
* 1,3-Dioxol-4-en-2-one, 1084
† Dipropyl ether, 2538
† Divinyl ether, 1516
1-Ethoxy-2-propyne, 1903
2-Ethoxyethanol, 1696
† Ethyl isopropyl ether, 2006
† Ethyl propenyl ether, 1950
† Ethyl vinyl ether, 1605
2-Ethylacryladehyde oxime, 1927
† 2-Ethylbutanal, 2481
† 2-Ethylhexanal, 3045
2-Furaldehyde, 1830
† Furan, 1435
4,5-Hexadien-2-yn-1-ol, 2321
2,4-Hexadienal, 2377
2,5-Hexadiyn-1-ol, 2322
2-Hexenal, 2426
2-Indanecarboxaldehyde, 3282
† Isobutyraldehyde, 1606
† Isopropyl vinyl ether, 1951
2-Isopropylacrylaldehyde oxime, 2447
† Isovaleraldehyde, 1952
Limonene, 3331
1,5-*p*-Menthadiene, 3332
* Methoxy-1,3,5,7-cyclooctatetraene, 3143
2-Methoxyethanol, 1280
† 2-Methoxyethyl vinyl ether, 1967

† Methyl vinyl ether, 1217
† 2-3-Methyl-2-methylenebutanal, 2427
† 4-Methyl-2-pentanone, 2489
∗ 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate, 3758
† 2-Methyltetrahydrofuran, 1955
α-Pentylcinnamaldehyde, 3656
† Propionaldehyde, 1220
Sodium 5,8,11,14-eicosatetraenoate, 3803
Sodium ethoxyacetylide, 1474
1,1,2,3-Tetrachloro-1,3-butadiene, 1385
† Tetrahydrofuran, 1607
Tetrahydronaphthalene, 3294
† Tetrahydropyran, 1959
Tridecanal, 3613
† Vinyl acetate, 1527
† 4-Vinylcyclohexene, 2999
See Indane-2-aldehyde
ACETYLENIC COMPOUNDS
ALKALI METALS
ALKENES
ALKYNES
BENZYL COMPOUNDS
DIENES
HALOALKENES
OXIMES
TETRAHYDROPYRANYL ETHER DERIVATIVES

PEROXOACIDS EOOH

Inorganic acids with a peroxide function are given the IUPAC name above, which distinguishes them from the organic PEROXYACIDS. Collectively they are a group of very powerful oxidants, individual compounds being:
Peroxodisulfuric acid, 4476
Peroxomonophosphoric acid, 4501
Peroxomonosulfuric acid, 4475
Peroxonitric acid, 4431

PEROXOACID SALTS EOO^-, MOO^-

Many of the salts of peroxoacids are unstable or explosive, are capable of initiation by heat, friction or impact, and all are powerful oxidants. Individually indexed compounds are:
Ammonium hydroxyoxodiperoxochromate(1—), 4224
Ammonium pentaperoxodichromate(2—), 4241
Ammonium peroxoborate, 0146
Ammonium peroxodisulfate, 4571
Ammonium tetraperoxochromate(1—), 4226

Calcium peroxodisulfate, 3934
Calcium triperoxochromate, 3939
Mercury(II) peroxybenzoate, 3630
Potassium diperoxomolybdate, 4654
Potassium diperoxoorthovanadate, 4662
Potassium hydrogen peroxomonosulfate, 4424
Potassium hydroxyoxodiperoxochromate(1—), 4221
Potassium *O*—*O*-benzoylmonoperoxosulfate, 2680
Potassium pentaperoxodichromate, 4243
Potassium peroxodisulfate, 4663
Potassium peroxoferrate(2—), 4390
Potassium tetraperoxochromate(3—), 4229
Potassium tetraperoxomolybdate, 4655
Potassium tetraperoxotungstate, 4664
Potassium tricyanodiperoxochromate(3—), 1041
Silver peroxochromate, 0037
Sodium monoperoxycarbonate, 0551
Sodium peroxoborate, 0155
Sodium peroxodisulfate, 4803
Sodium peroxyacetate, 0776
Sodium peroxydicarbonate, 1020
Sodium tetraperoxochromate(3—), 4234
Sodium tetraperoxomolybdate, 4710
Sodium tetraperoxotungstate, 4804
Tetramethylammonium pentaperoxodichromate, 3097
Thallium hydroxyoxodiperoxochromate(1—), 4222
Thallium(I) peroxodiborate, 0171
See other OXIDANTS

PEROXOCHROMIUM COMPOUNDS

1. Pope, M. T. *et al., Chem. Rev.*, 1994, **94**(3), 576
2. Editor's comments

Most solid peroxochromates explode when heated or struck, some are reported to explode spontaneously at room temperature. Few have been isolated and fully characterised. Assigned structures are sometimes doubtful [1], especially when questionable primary sources have been reinterpreted by secondary and tertiary reviews. A wide and confused selection of peroxochromate salts is to be found in the literature. It seems probable that there are, in fact, only two main series: the red tetraperoxochromate(3—) salts most of which explode only when provoked by heat or strong acid, and those of a more sensitive blue mono-anion, probably hydroxyoxodiperoxychromate(1—) which just explode. The latter series have an anhydride, CrO_5, which may be isolated as relatively stable complexes with electron donors such as methanol or pyridine. Both series are made by treating chromium(VI) species with hydrogen peroxide, at differing pH, and may be interconverted [2]. There is also a mostly neutral group, generally shock and heat sensitive, of diperoxochromium compounds with three donor ligands [1]. A great many others will be found in this work, mostly the result of mistaken identity due to poor analysis. For individual peroxochromate salts and neutral complexes:

See entry AMMINECHROMIUM PEROXOCOMPLEXES, PEROXOACID SALTS

PEROXO-TRANSITION METAL COMPOUNDS

1. Pope, M. T. *et al., Chem. Rev.*, 1994, **94**(3), 576
2. Guerchais, J. E. *et al, J. Mol. Catal.*, 1980, **7**, 141
3. Hou, S-Y. *et al., Inorg. Chem. Comm.*, 2003, **6**(9), 1246

Chromium compounds are covered above. Most tetraperoxomolybdates(2-) and tetraperoxotungstates(2-) explode when heated or struck [1]. An acetate bridged bis-diperoxomolybdate(VI) exploded when heated [3]. Organoperoxoniobium compounds occasionally explode on exposure to air [2]. A peroxovanadate complex is reported seriously explosive.

See Diammonium Aquabis(peroxotartratovanadate)(2-)

See entry PEROXOACID SALTS

PEROXYACIDS RCO.OOH

1. Castrantas, 1965, 12; Swern, 1970, Vol. 1, 59, 337
2. Isard, A. *et al.*, Ger. Offen., 1 643 158, 1968
3. Isard, A. *et al., Chemical Tech.*, 1974, **4**, 380
4. Swern, D., *Chem. Rev.*, 1945, **45**, 3—16
5. Augustine, 1969, 221, 217
6. Payne, G. B., *J. Org. Chem.*, 1962, **27**, 628
7. Augustine, 1971, 164

The peroxyacids were until relatively recently the most powerful oxidants of all organic peroxides, and it is often unnecessary to isolate them from the mixture of carboxylic acid and hydrogen peroxide used to generate them. The pure lower aliphatic members are explosive (performic, particularly) at high, but not low, concentrations, being sensitive to heat but not usually to shock. Dipicolinic acid or phosphates have been used to stabilise these solutions. The detonable limits of peroxyacid solutions can be plotted by extrapolation from known data. Aromatic peroxyacids are generally more stable, particularly if ring substituents are present [1].

The patented preparation of peroxyacids [2] by interaction of carboxylic acids with hydrogen peroxide in presence of metaboric acid needs appropriate safeguards to prevent accidental separation of the conc. peroxyacids [3]. Much descriptive data on stabilities of a wide selection of peroxyacids has been summarised [4]. A general method of preparation of peroxyacids involving addition of e.g. the anhydrides of acetic, maleic, phthalic or trifluoroacetic acids to a suspension of 90% hydrogen peroxide in dichloromethane with a drop of sulfuric acid, which although it contravenes the rule of adding concentrated hydrogen peroxide to the substrate (rather than the reverse), is nevertheless preferred because it minimises handling of concentrated peroxide, and avoids the possibility of its contact with stopcock grease [5]. However, the mixture of 90% hydrogen peroxide and dichloromethane is reported to be shock-sensitive [6]. In metal-ion catalysed oxidations by peroxyacids, it is necessary to avoid metal catalysed decomposition of the peroxy acid. Traces of transition metal ions (cobalt, iron, manganese, nickel or vanadium) can lead to explosively violent decomposition of lower aliphatic peroxyacids (peroxy-formic, -acetic, -pivalic, -trifluoroacetic acids), even at concentrations of 25% in inert solvents. Maintenance of high-dilution conditions will prevent such runaway reactions [7]. Individually indexed peroxyacids are:

Benzeneperoxyseleninic acid, 2330
Benzeneperoxysulfonic acid, 2334
3-Chloroperoxybenzoic acid, 2672
Diperoxyazelaic acid, 3183
Diperoxyterephthalic acid, 2920
Monoperoxysuccinic acid, 1537
Peroxyacetic acid, 0833
Peroxybenzoic acid, 2729
3-Peroxycamphoric acid, 3342
Peroxycrotonic acid, 1530
Peroxyformic acid, 0419
Peroxyfuroic acid, 1831
Peroxyhexanoic acid, 2508
Peroxypropionic acid, 1232
Peroxytrifluoroacetic acid, 0662
Trichloroperoxyacetic acid, 0655
POLYMERIC PEROXYACIDS
See I,I-DI(BENZOYLPEROXY)ARYLIODINES
See also ORGANIC PEROXIDES

PEROXYCARBONATE ESTERS —OCO.OOR, —OOCO.OOR

1. Strain, F. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 1254
2. Kirk-Othmer, 1967, Vol. 14, 803

Of the 3 possible types of peroxycarbonate esters —dialkyl monoperoxycarbonates, dialkyl diperoxycarbonates and dialkyl peroxydicarbonates—, the latter are by far the least stable group. Several of the 16 alkyl and substituted-alkyl esters prepared decomposed violently or explosively at temperatures only slightly above the temperature of preparation (0—10°C), owing to self-accelerating exothermic decomposition. Several were also explosive on exposure to heat, friction or shock [1]. Amines and certain metals cause accelerated decomposition of dialkyl peroxydicarbonates by a true catalytic mechanism [2]. Individually indexed compounds are:

Bis(2-methoxyethyl) peroxydicarbonate, 3032
O—O-tert-Butyl isopropyl monoperoxycarbonate, 3046
Diallyl peroxydicarbonate, 2984
Di-*tert*-butyl diperoxycarbonate, 3188
Didodecyl peroxydicarbonate, 3859
Diethyl peroxydicarbonate, 2440
Diisopropyl peroxydicarbonate, 3029

Dimethyl peroxydicarbonate, 1539
Dipropyl peroxydicarbonate, 3030
See other PEROXIDES

PEROXY COMPOUNDS **C—OO—**

Castrantas, 1965

Detonation theory is used to clarify the explosive characteristics of peroxy compounds. Some typical accidents are described. Hazards involved in the use of a large number of peroxy compounds (including all those then commercially available) are tabulated, with 134 references.

PEROXYESTERS **—CO.OOR**

Castrantas, 1965, 13; Swern, 1970, Vol. 1, 79

Although as a group the peroxyesters are noted for instability, there is a fairly wide variation in stability between particular sub-groups and compounds.

and the individually indexed compounds:

1,1-Bis(4-nitrobenzoylperoxy)cyclohexane, 3794
1,1-Bis(benzoylperoxy)cyclohexane, 3798
Bis(trimethylsilyl) peroxomonosulfate, 2598
tert-Butyl 1-adamantaneperoxycarboxylate, 3685
tert-Butyl 4-nitroperoxybenzoate, 3394
tert-Butyl chloroperoxyformate, 1920
tert-Butyl diperoxyoxalate, 3350
O—O-tert-Butyl hydrogen monoperoxymaleate, 3010
tert-Butyl peroxyacetate, 2503
† *tert*-Butyl peroxybenzoate, 3397
tert-Butyl peroxynitrate, 1657
* Butyryl peroxonitrate, 1569
Di-*tert*-butyl diperoxycarbonate, 3188
Di-*tert*-butyl diperoxyphthalate, 3709
† 1,1-Dichloroethyl peroxyacetate, 1487
Fluorocarbonylperoxonitrate, 0337
1-Hydroxyethyl peroxyacetate, 1621
† Isobutyl peroxyacetate, 2506
* Pentafluorosulfur peroxyacetate, 0752
* Peroxyacetyl nitrate, 0762
* Peroxyacetyl perchlorate, 0733
* Peroxypropionyl nitrate, 1183
* Poly(peroxyisobutyrolactone), 1531
1,1,6,6-Tetrakis(acetylperoxy)cyclododecane, 3804
7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione, 3343
Trichloromethyl peroxyacetate, 1094
Trifluoromethyl 3-fluorocarbonylhexafluoroperoxybutyrate, 2054
Trifluoromethyl peroxonitrate, 0345
Trifluoromethyl peroxyacetate, 1100

I,I-DI(BENZOYLPEROXY)ARYLIODINES
PEROXYCARBONATE ESTERS
See TERT-BUTYL PEROXOPHOSPHATE DERIVATIVES

PETROLEUM COKE

1. Hulisz, S., *Chem. Abs.*, 1977, **86**, 19269
2. Statkov, O. P. *et al., Chem. Abs.*, 1989, **110**, 62453

The flammability and explosivity of high-sulfur petroleum coke dust (particle size < 75 μm) were examined. Air-dried powder was non-explosive but fire-prone above 400°C. A 5 mm layer became incandescent at 420—470° and a dust cloud ignited at 520—660°C [1]. The fire and explosion hazards of petroleum coke or anthracite, when used in the manufacture of furnace electrodes, may be reduced by heat treatment [2].
See Carbon
See also CARBONACEOUS DUSTS

PHASE CHANGES

1. Adams, R. *et al., Org. Synth. Coll. I*, 1944, 94
2. Editor's comments

These can be a source of hazard during reaction. A very few phase changes are energetic enough to be a hazard in their own right. Commonly the effect is more subtle. Some reactions are performed near boiling point in a solution; if the product supersaturates and then suddenly crystallises the result will be explosive boiling. The classic benzoin preparation [1] is an example of this. In other cases supersaturation by a gaseous co-product is possible, crystallisation may then nucleate gas evolution and once again the reaction mixture leaves the pot. In yet others, separation of a new liquid phase changes the kinetics of reaction which may markedly accelerate. This is often seen in preparation of substituted triphenylmethyl chlorides by the Friedel Crafts route, some of which also show gas supersaturation and intermediate crystallisation [2].

Phase change problems are seldom predictable but, once recognised, can usually be controlled by slowing the charge rate of reagent(s) and changing the temperature of reaction, down if heat of crystallisation is the problem, but possibly up for the other phenomena.

α-PHENYLAZO HYDROPEROXIDES —C(OOH)N=NPh

1. Swern, 1971, Vol. 2, 19
2. Busch, M. *et al., Ber.*, 1914, **47**, 3277
3. Baumstark, A. L. *et al., J. Org. Chem.*, 1983, **48620**, 69
4. Tezuka, T. *et al., J. Chem. Soc., Perkin Trans. 1*, 1984, 2509
5. Tezuka, T. *et al., Chem. Lett.*, 1986, 1671—1674

Alkyl- and aryl-hydrazones of aldehydes and ketones readily peroxidise in solution and rearrange to azo hydroperoxides [1], some of which are explosively unstable [2]. Dry samples of the *p*-bromo- and *p*-fluoro-hydroperoxybenzylazobenzenes, prepared by oxygenation of benzene solutions of the phenylhydrazones, exploded while on filter paper in the dark, initiated by vibration of the table or tapping the paper. Samples were later stored moist with benzene at —60°C to prevent explosion [3]. A series of α-phenylazo hydroperoxides derived from the phenyl- or *p*-bromophenyl-hydrazones of acetone, acetophenone or cyclohexanone, and useful for epoxidation of alkenes, are all explosive [4]. The stability of several substituted phenylazo hydroperoxides was found to be strongly controlled by novel substituent effects [5].

Individually indexed compounds are:

2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3150
α-(4-Bromophenylazo)benzyl hydroperoxide, 3600
α-(4-Bromophenylazo)phenylethyl α-hydroperoxide, 3641
1,2-Dihydroperoxy-1,2-bis(benzeneazo)cyclohexane, 3756
α-Phenylazo-4-bromobenzyl hydroperoxide, 3601
α-Phenylazo-4-fluorobenzyl hydroperoxide, 3602
α-Phenylazobenzyl hydroperoxide, 3603
1-Phenylazocyclohexyl hydroperoxide, 3533
* 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3H)pyrazole, 3835

PHOSPHINES RPH_2, R_2PH

Halogens

Van Wazer, 1958, Vol. 1, 196

Organic derivatives of phosphine react very vigorously with halogens

Individually indexed (unsubstituted) phosphines are:

* Cobalt tris(dihydrogenphosphide), 4197
* *N,N′*-Di-*tert*-butyl-*N,N′*-bis(trimethylsilyl)diaminophosphene, 3668
† Diphosphane, 4533
* Potassium dihydrogenphosphide, 4454
* Sodium dihydrogen phosphide, 4468
* Tetrakis(trimethylsilyl)diaminodiphosphene, 3582
* Trimethylgermylphosphine, 1328
* Trisilylphosphine, 4578
* Tris(iodomercurio)phosphine, 4609
* *N,N,N′*-Tris(trimethylsilyl)diaminophosphine, 3226

PHOSPHORUS COMPOUNDS

Groups falling within this class are:

ALKYLHALOPHOSPHINES
ALKYLPHOSPHINES
tert-BUTYL PEROXOPHOSPHATE ESTERS
N-CHLORINATED PHOSPHORUS AMIDES
HALOPHOSPHINES
METAL PHOSPHINATES
METAL PHOSPHORUS TRISULFIDES
NON-METAL OXIDES
NON-METAL SULFIDES
PHOSPHINES
PHOSPHORUS ESTERS

PHOSPHORUS ESTERS $(RO)_3P$, $(RO)_3P{:}O$, $(RO)_2P(S)SR'$ etc.

1. Anon., *Loss Prev. Bull.*, 1979, (030), 159—160
2. *See entry* SELF-ACCELERATING REACTIONS
3. Lhomme, V. *et al., Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, 98—102
4. Kirk-Othmer, 1982, Vol. 17, 495

Two incidents involving thermal decomposition of an unspecified phosphorus ester insecticide which unintentionally became heated to 150—160°C are described. In one case the overheating arose from a relatively slow exotherm occurring at 90—100°C, and in the second, material at 55°C was heated instead of being cooled [1]. A number of phosphate and thiophosphate esters are of limited thermal stability and undergo highly exothermic self-accelerating decomposition reactions which may be further catalysed by impurities. The potential hazards can be reduced by appropriate thermal control measures. An example is the substitution of hot water at 60°C for pressurised steam to melt a solid phosphate ester, which on adiabatic calorimetric examination was found to have a time to maximum decomposition rate of 6 h at 110° but 11 h at 100°C [2]. The combined use of vapour phase pyrolysis to decompose various phosphorus esters, and of GLC and mass spectrometry to analyse the pyrolysis products, allowed a thermal degradation scheme to be developed for phosphorus esters [3]. Phosphite esters are prone to the Arbuzov rearrangement to phosphonate esters. This is seriously exothermic and can accelerate to explosion if conducted thermally. The halide catalysed variant, at lower temperatures, with rate governed by catalyst, is preferred [4].

Individually indexed compounds are:
Allyl phosphorodichloridite, 1165
Bis(trimethylsilyl) phosphonite, 2607
O—O-tert-Butyl di(4-tolyl) monoperoxophosphate, 3757
O—O-tert-Butyl diphenyl monoperoxophosphate, 3706
Diallyl phosphite (Di-2-propenyl phosphonite), 2450
Dibenzyl phosphite, 3651
Dibenzyl phosphorochloridate, 3643
Dibutyl hydrogen phosphite, 3080
Diethyl 4-nitrophenyl phosphate, 3323
Diethyl 4-nitrophenyl thionophosphate, 3322
Diethyl ethanephosphonite, 2567
Diethyl phosphite, 1727
* Diethyl phosphorochloridate, 1675
Dimethyl 2-chloro-4-nitrophenyl thionophosphate, 2955
Dimethyl 3-chloro-4-nitrophenyl thionophosphate, 2956
Dimethyl 4-nitrophenyl thionophosphate, 2974
Dimethyl ethanephosphonite, 1726
* Dimethyl hydrazidophosphate, 0955
Dimethyl *N,N*-dichlorophosphoramidate, 0897
Dimethyl phosphoramidate, 0948
O,O-Dimethyl *S*-methylcarbamoylmethyl phosphorodithioate, 2003
* 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclooctane, 2543
Di(*O*—*O*-tert-butyl) ethyl diperoxophosphate, 3368

- * Diphenyl azidophosphate, 3483
- * Potassium *O,O*-diphenyl dithiophosphate, 3475
- * Pyrocatecholato(2-)(quinolin-8-olato-*N,O*)-trioxygenido(2-)phosphorus, 3671
- Triallyl phosphate, 3178
- Trimethyl phosphate, 1314
- Trimethyl phosphite, 1311
- Trimethyl thiophosphate, 1312

PHYTOSTEROLS (several compounds and isomers)

Dry and finely divided phytosterol materials are a significant dust explosion hazard. *See entry* DUST EXPLOSION INCIDENTS (reference 22)

PICRATES $(O_2N)_3C_6H_2O^-$

1. Anon., *Angew. Chem. (Nachr.)*, 1954, **2**, 21
2. Hopper, J. D., *J. Franklin Inst.*, 1938, **225**, 219—225
3. Kast, H., *Chem. Abs.*, 1911, **5**, 2178
4. Nakamura, K. *et al., Bull. Chem. Soc. Japan*, 1987, **60**, 2037—2040
5. Matzukawa, M. *et al., Science & Technology of Energetic Materials*, 2003, **64**(5), 183

While the m.p. of a picrate was being determined in a silicone oil bath approaching 250°C, an explosion occurred, scattering hot oil. It is recommended that picrates, styphnates and similar derivatives should not be heated above 210°C in a liquid-containing m.p. apparatus [1]. In an investigation of the sensitivity to impact of a range of hydrated and anhydrous metal picrates, anhydrous nickel picrate was found to be particularly sensitive [2]. The explosive characteristics of a range of 13 mono- to tri-valent metal picrates and methylpicrates was determined [3]. The hydrated picrates of the lanthanide (rare-earth) metals were prepared from the carbonates. Dysprosium and ytterbium gave octahydrates, while lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium gave undecahydrates, all being stable to drying in air. Drying under vacuum, by desiccation, or by warming just above 30°C could, however, give the anhydrous picrates, of which the explosion temperatures were all above 300°C [4]. A study of all five alkali metal picrates (obtained as hydrates), by DSC and thermogravimetry, showed them thermally more stable than the parent acid, but also more shock sensitive [5].

Individually indexed compounds are:

- Ammonium picrate, 2315
- Calcium picrate, 3424
- * Cobalt(II) picramate, 3454
- Copper(II) picrate, 3426
- Lanthanum picrate, 3735
- Lead(II) picrate, 3430
- Manganese picrate hydroxide, 3736
- Mercury(II) picrate, 3427
- *S*-7-Methylnonylthiouronium picrate, 3731
- Nickel picrate, 3429

Potassium picrate, 2078
Sodium picrate, 2079
2,2,4-Trimethyldecahydroquinolinium picrate, 3759
Zinc picrate, 3431

See also ARENECYCLOPENTADIENYLIRON(II) PICRATES

PLANT CLEANING INCIDENTS

1. Anon., *Loss Prev. Bull.*, 1980, (035), 7—11; 1981, (038), 23—27
2. Peischel, M., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 721—731, Heidelberg, ISSA, 1987

The need to provide both detailed instructions and proper supervision for plant cleaning operations, either before maintenance operations in any plant, or between different product runs in multi-use batch plant, is stressed. Several examples are given of untoward reactions and incidents which occurred when either or both of the above requirements were lacking. The importance of checking the effectiveness of cleaning operations before restarting plant was highlighted by further examples of incidents [1]. During cleaning of a 6 m^3 tank by pump-recycled solvent mixture, electrostatic sparks ignited the vapour—air mixture and blew off the tank lid [2].

Some individually indexed examples will be found under:

Nitric acid, 4430
Nitric acid, : Alcohols, 4430
Nitric acid, : Polyurethane foam, 4430
Nitric acid, : Resorcinol, 4430
Phosphoryl chloride, : Water, 4143

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

PLATINUM COMPOUNDS

Cotton, F. A., *Chem. Rev.*, 1955, **55**, 577

Several platinum compounds, including trimethylplatinum derivatives, are explosively unstable. Some compounds of the other platinum group metals are also of limited stability. Individually indexed compounds are:

Amminedecahydroxydiplatinum, 4588
Amminepentahydroxyplatinum, 4566
Ammonium hexachloroplatinate, 4180
Ammonium tetranitroplatinate(II), 4573
Diacetatoplatinum(II) nitrate, 1507
Diamminedichloroamidotrichloroplatinum(IV), 4173
* Diamminedihydroxyosmium, 4567
* Diamminepalladium(II) nitrate, 4557
* Diamminepalladium(II) nitrite, 4554
cis-Diammineplatinum(II) nitrite, 4555
* Dodecamethyltetraplatinum(IV) azide, 3584
* Dodecamethyltetraplatinum(IV) perchlorate, 3581
Hexamethyldiplatinum, 2602
* Palladium(II) acetate, 1536

* Palladium(III) oxide, 4842
* Palladium(IV) oxide, 4829
* Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3772
Platinum(IV) oxide, 4830
* Potassium dinitrooxalatoplatinate(2—), 0984
Potassium hexaazidoplatinate(IV), 4660
Potassium hexachloroplatinate, 4181
Sodium hexahydroxyplatinate(IV), 4559
Tetraamminehydroxynitratoplatinum(IV) nitrate, 4589
* Tetraamminepalladium(II) nitrate, 4583
Tetraammineplatinum(II) nitrate, 4583
* *N,N,N′*, N′-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) iodide, 3220
* *N,N,N′*,N′-Tetramethylethane-1,2-diamine,trimethylpalladium(IV) bromide, 3219
Tetramethylplatinum, 1762
Triamminenitratoplatinum(II) nitrate, 4577
Trimethylplatinum hydroxide, 1325
See also GOLD COMPOUNDS
See other HEAVY METAL DERIVATIVES

PLATINUM GROUP METALS

Ullmann, 1992, Vol. A21, 125/6

A section on explosion hazards is included in the monograph on platinum group metals. Most of the hazards are associated with their activity as redox catalysts and are already covered in this work. Warning is given of violent alloy formation with e.g. lithium and titanium, especially by platinum and ruthenium. Alloys, or compounds, with metalloids may also be formed energetically. Absorption and sudden release of hydrogen, which will then be ignited by the catalytic metal (itself pyrophoric if finely divided) is a frequent hazard, worst for ruthenium which can retain more hydrogen than the others. Compounds and complexes incorporating both oxidant anions and oxidisable ligands (ammonia, organic moieties etc.) are likely to prove shock sensitive explosives.

See AMMINEMETAL OXOSALTS, ORGANOMETALLIC NITRATES

POLY(AMINIUM) PERCHLORATES $[\text{-}(CH_2)_mN^+H_{2-}\text{-}]^n\ nClO_4^-$

Thomas, T. J. *et al., Amer. Inst. Aero. Astron. J.*, 1976, **14**, 1334—1335

Ignition temperatures were determined by DTA for the perchlorate salts of ethylamine, isopropylamine, 4-ethylpyridine, poly(ethyleneimine), poly(propyleneimine), and poly(2- or 4-vinylpyridine). In contrast to the low ignition temperatures (175—200°C) of the polymeric salts, mixtures of the polymeric bases with ammonium perchlorate decompose only above 300°C.

See AMINIUM PERCHLORATES
See other PERCHLORATE SALTS OF NITROGENOUS BASES

POLYAZACAGED METAL PERCHLORATES

Harrowfield, J. MacB. *et al., Inorg. Synth.*, 1980, **20**, 85—86

A wide range of macrocyclic or multicyclic polynitrogen 'cage' ligands have been prepared in recent years and used to study the metal ion shielding and other effects of deep complexing of metal salts. In several cases it is known that the perchlorate salts of such complexes are highly unstable or explosive, and it must be assumed that this is a likely generality for the majority of such perchlorate salts. There are separate entries with specific warnings for the groups CLATHROCHELATED METAL PERCHLORATES, [14] DIENE-N_4 COMPLEXES, TETRAAZAMACROCYCLANEMETAL PERCHL-ORATES, and TETRAMETHYL[14]TETRAENE-N_8 METAL PERCHLORATES but the 'Sepulchrate' metal complexes (of the reference above) of 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-eicosane ('Bicyclo[6.6.6]ane-1,3,6,10,13,16,19,-N_8') are also likely to give unstable perchlorate salts.

CLATHROCHELATED METAL PERCHLORATES
[14] DIENE-N_4 COMPLEXES
TETRAAZAMACROCYCLANEMETAL PERCHLORATES
TETRAMETHYL[14]TETRAENE-N_8 METAL PERCHLORATES
See other AMMINEMETAL OXOSALTS

POLYCONDENSATION REACTION INCIDENTS

A number of runaway reaction incidents which have involved the formation of polymeric species differ from usual polymerisation reactions of monomers in that elimination reactions of various types have been involved. Individually indexed examples are:

2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one, 2803
Benzyl alcohol, : Hydrogen bromide, Iron, 2802
Benzyl bromide, : Molecular sieve, 2731
Benzyl chloride, : Catalytic impurities, 2734
Benzyl fluoride, 2742
1,2-Bis(chloromethyl)benzene, 2941
Ethylene oxide, : Contaminants, 0825
Furoyl chloride, 1812
4-Methoxy-3-nitrobenzoyl chloride, 2911
See other UNIT PROCESS OR UNIT OPERATION INCIDENTS
See related POLYMERISATION INCIDENTS

POLY(DIMERCURYIMMONIUM) COMPOUNDS $(Hg{=}N^+{=}Hg\ Z^-)_n$

1. Ciusa, W., *Chem. Abs.*, 1943, **37**, 3271.9; 1944, 38, 4133.4
2. Sorbe, 1968, 97
3. Bailar, 1973, Vol. 3, 313

Several explosive salts including the acetylide, azide, borate, bromate, chlorate, chromate, iodate (and ammonium iodate double salt), nitrite, perchlorate (and ammonium perchlorate double salt), periodate, permanganate, picrate and trinitrobenzoate were prepared. The 3 latter salts and the acetylide, azide and bromate are impact-sensitive detonators [1]. It appears probable that many of the explosively unstable

compounds [2], formed in various ways from interaction of mercury or its compounds with ammonia or its salts, may have the common polymeric structure now recognised for Millon's base [3]. This is a silica-like network of N^+ and Hg in 4- and 2-coordination, respectively, with OH^- and water in the interstitial spaces. Individually indexed compounds are:
Poly(dimercuryimmonium acetylide), 0665
Poly(dimercuryimmonium azide), 4606
Poly(dimercuryimmonium bromate), 0253
Poly(dimercuryimmonium hydroxide), 4416
Poly(dimercuryimmonium iodide hydrate), 4449
Poly(dimercuryimmonium perchlorate), 4006
Poly(dimercuryimmonium permanganate), 4603
See other MERCURY COMPOUNDS, N-METAL DERIVATIVES

POLY(DIMETHYLSILYL)CHROMATE $[Me_2SiOCrO_2O]_n$

See Bis(trimethylsilyl) chromate

POLYMERIC PEROXYACIDS

1. Takagi, T. J., *Polymer Sci. (B), Polymer Lett.*, 1967, **5**, 1031—1035
2. Harrison, C. R. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 1009
3. Oshike, Y. *et al., Chem. Abs.*, 1987, **107**, 59502

An ion exchange resin based on poly-acrylic or -methacrylic acids and containing aliphatic peroxyacid groups [1] readily explodes on impact, but a polystyrene resin containing aromatic peroxyacid groups on ~70% of the phenyl residues could not be caused to explode on impact [2]. Polymeric peroxides formed from sodium peroxide and the acid chlorides of dibasic acids show poor solubility in monomers and solvents and poor safety characteristics in handling. However, the polymeric peroxides formed from the acid chlorides derived from oligo-esters of adipic acid and ethylene glycol are better in these respects [3].
See 2,2′-Azobis(2-amidiniopropane) peroxodisulfate
See PEROXYACIDS

POLYMERISATION INCIDENTS

1. Anon., *CISHC Chem. Safety Summ.*, 1978, **49**(194), 32, 33
2. Schmidt, C. U. *et al., Chem. Eng. Sci.*, 1988, **43**, 2133—2137
3. King, 1991, 56
4. *Chemical Reaction Hazards,*, Barton, J. & Rogers, R., Rugby, IChE, 1993
5. Rowe, S. M., 1994, personal communication.
6. Frurip, D. J., *et al., Process Safety Progress*, 1995, **14**(2), 79
7. Maschio, G. *et al., Chem. Eng. Sci.*,1999, **54**(15-16), 3273
8. Editor's comments, 1998
9. U.S. Chemical Safety and Hazard Investigation Board, 2001, Report 2001-03-I-GA

In a first full scale attempt at a new polymerisation process, the thermally unstable initiator was charged and heated to reaction temperature, but there was then an unforeseen delay of an hour before monomer addition was started. The rate of polymerisation effected by the depleted initiator was lower than the addition rate of the monomer, and the concentration of the latter reached a level at which an uncontrollable polymerisation set in which eventually led to pressure-failure of the vessel seals. Precautions to prevent such occurrences are detailed. In another incident, operator error led to catalyst, condensing styrene and acrylonitrile being ducted into an unstirred weighing tank instead of a reactor. When the error was recognised, the reacting mixture was dropped into drums containing inhibitor. One of the sealed drums had insufficient inhibitor to stop the reaction, and it slowly heated and eventually burst [1]. The features and use of a specially developed polymerisation reaction safety calorimeter to study critical polymerisation conditions are described [2]. Conditions and incidents for runaway polymerisation of a number of monomers are given [3]. Polymerisation has latterly overtaken nitration as the leading source of runaway reactions in the British chemical industry [4]. Runaway free-radical polymerisations can be suppressed by injection of a sub-percentage quantity of appropriate free radical traps, such as the anti-oxidants phenothiazine or butylcatechol. Note that this cannot be expected to inhibit condensation polymerisations, such as that of phenol and formaldehyde, which also are a common cause of accident [5]. Procedures for testing monomers for hazardous polymerisation potential have been devised [6]. Application of calorimetric methods to safe scale-up of polymerisation is described, using that of methyl methacrylate as the model [7]. It is not necessary to have an exothermic reaction for explosion – an account is given of a minor, but fatal, explosion due to slow degradation of a hot polymer product, generating volatiles, the vent having become plugged by the polymer [9].

Stabilisation of unsaturated monomers for storage is a complex phenomenon; acrylates, especially, are partially stabilised by atmospheric oxygen. The anti-oxidants added as stabilisers merely prevent the peroxides produced when oxygen terminates a radical chain from themselves subsequently acting as radical initiators. Acrylates stored with exclusion of air may polymerise violently even though stabilised. Since the core of a crystal will not hold any stabiliser, and probably no oxygen, melting solid monomers produces microdomains well set-up for polymerisation, which may warm the bulk to a temperature where thermal polymerisation becomes unstoppable. Melting frozen monomers, such as acrylamide or acrylic and methacrylic acids, has been a frequent cause of mishap [8].

Other polymerisation incidents are:

† Acrylaldehyde, 1142
Acrylamide, 1176
Acrylic acid, 1145
Acrylic acid, : Initiator, Water, 1145
† Acrylonitrile, 1104
† Acrylonitrile, : Initiators, 1104
† Acrylonitrile, : Silver nitrate, 1104
† Acryloyl chloride, 1090
Allyl 4-toluenesulfonate, 3309
Aluminium chloride, : Alkenes, 0062
3-Aminopropiononitrile, 1208

† Aziridine, : Acids, 0859
2,2′-Azobis(2-amidiniopropane) chloride, 3083
† 1,3-Butadiene, 1476
† 1,3-Butadiyne, : Arsenic pentafluoride, 1381
2-Buten-1-yl benzenesulfonate, 3310
† 1-Buten-3-one, 1512
† 2-Chloro-1,3-butadiene, 1447
† 1-Chloro-2,3-epoxypropane, : Contaminants, 1158
2-Chloroethylamine, 0892
2-Chloroethylammonium chloride, : Alkali, 0936
† Chloroethylene, 0726
Chloroperoxytrifluoromethane, : Tetrafluoroethylene, 0318
Cyanamide, : Water, 0403
2-Cyanoethanol, : Acids, or Bases, 1177
Cyanogen fluoride, : Hydrogen fluoride, 0337
† Cyclopentadiene, 1851
† Cyclopentadiene, : Potassium hydroxide, 1851
1,2-Di(3-buten-1-ynyl)cyclobutane, 3503
Diallyl phosphite, 2450
Diallyl sulfate, 2437
† 1,1-Dichloroethylene, 0691
1,4-Dicyano-2-butene, 2304
Diisocyanatomethane, : Dimethylformamide, 1076
† Diketene, : Acids, or Bases, or Sodium acetate, 1437
2,3-Epoxypropionaldehyde oxime, 1178
† Ethyl acrylate, 1907
† Ethylene oxide, 0825
† Formaldehyde, : Phenol, 0415
6-Fulvenoselone, 2209
Furfuryl alcohol, 1874
Glycolonitrile, 0757
2,4-Hexadienal, 2377
† Hydrogen cyanide, 0379
4-Hydroxy-*trans*-cinnamic acid, 3130
N-Hydroxymethylacrylamide, 1566
Methacrylic acid, 1525
† Methyl acrylate, 1526
† Methyl methacrylate: Propionaldehyde, 1909
† Methyl vinyl ether: Acids, 1217
1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene, 3754
3-Methyl-2-penten-4-yn-1-ol, 2378
† 2-Methylaziridine: Acids, 1253
Nitrilotris(oxiranemethane), 3175
2-Nitropropene, 1179
Octakis(trifluorophosphine)dirhodium, : Acetylenic esters, 4381
Phenylacetylene, 2907

† 2-Propen-1-ol, : Sulfuric acid, 1219
† Propene, : Lithium nitrate, Sulfur dioxide, 1194
Propiolaldehyde, 1082
† Propylene oxide, : Sodium hydroxide, 1221
3-Propynethiol, 1148
3-Propynol, : Mercury(II) sulfate, Sulfuric acid, Water, 1144
Styrene, : Air, Polymerising styrene, 2940
Styrene, : Butyllithium, 2940
Styrene, : Dibenzoyl peroxide, 2940
Styrene, : Initiators, 2940
† Tetrafluoroethylene, 0624
2,2,3,3-Tetrafluoropropanol, : Potassium hydroxide, or Sodium, 1130
Thiocyanogen, 0997
1,3,5-Triethynylbenzene, 3437
† Vinyl acetate, 1527
Vinylpyridine, 2755
See ACRYLIC MONOMERS
See also VIOLENT POLYMERISATION
See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

POLYNITROALKYL COMPOUNDS **$C(NO_2)_n$, $O_2NC—CNO_2$**

1. Hammond, G. S. *et al., Tetrahedron*, 1963, **19**(Suppl. 1), 177, 188
2. Grakauskas, V. *et al., J. Org. Chem.*, 1978, **43**, 3485—3488

Trinitromethane (‘nitroform’), dinitroacetonitrile, their salts and polynitroalkanes are all potentially dangerous, and must be carefully handled as explosive compounds [1]. Many congeners and derivatives of dinitromethane are explosive and require careful and appropriate handling [2]. Individually indexed compounds are:
N,N′-Bis(2,2,2-trinitroethyl)urea, 1869
* Borane—bis(2,2-dinitropropylhydrazine), 0137
Dichlorodinitromethane, 0327
* *N*-Dimethylethyl-3,3-dinitroazetidine, 2844
2,3-Dinitro-2-butene, 1506
1,1-Dinitro-3-butene, 1505
Dinitroacetonitrile, 0672
* 3,3-Dinitroazetidinium trifluoromethanesulfonate, 1491
Dinitrodiazomethane, 0542
5(1,1-Dinitroethyl)-2-methylpyridine, 2960
Dinitromethane, 0409
2,4-Dinitropentane isomers, 1947
2,2-Dinitropropylhydrazine, 0137
3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2397
2-Fluoro-2,2-dinitroethanol, 0747
Fluorodinitromethane, 0373
Fluorodinitromethyl azide, 0340
Fluorotrinitromethane, 0339

1,1,1,3,5,5,5-Heptanitropentane, 1848
Hexanitroethane, 1010
Lithium 1,1,2,2-tetranitroethanediide, 0990
Potassium 1,1,2,2-tetranitroethanediide, 0985
Potassium 1,1-dinitropropanide, 1171
Potassium dinitroacetamide, 0705
Potassium dinitromethanide, 0376
Potassium trinitromethanide, 0527
Silver cyanodinitromethanide, 0564
Silver dinitroacetamide, 0685
Silver trinitromethanide, 0301
Sodium 1,1,2,2-tetranitroethanediide, 1003
Sodium 2,2,2-trinitroethanide, 0709
Sodium 5-(dinitromethyl)tetrazolide, 0677
Sodium dinitroacetamide, 0708
Sodium dinitromethanide, 0383
Tetrakis(2,2,2-trinitroethyl) orthocarbonate, 3126
* 1,3,5,7-Tetranitroadamantane, 3304
Tetranitromethane, 0543
1,1,1-Triazidodinitroethane, 0679
Trinitroacetonitrile, 1005
1,1,1-Trinitroethane, 0771
2,2,2-Trinitroethanol, 0772
Trinitromethane, 0384
Tris(2,2,2-trinitroethyl) orthoformate, 2782
* 1,3,5-Tris(nitromethyl)benzene, 3139
See FLUORODINITROMETHYL COMPOUNDS, TRINITROETHYL ORTHOESTERS

POLYNITROARYL COMPOUNDS $Ar(NO_2)_n$

1. Urbanski, 1964, Vol. 1
2. Shipp, K. G. *et al., J. Org. Chem.*, 1972, **37**, 1966
3. Shipp, K. G. *et al.*, US Pat. 3 941 853, 1976
4. Zenor, S., *Thermochim. Acta*, 1979, **31**, 269—283
5. Zhang, H. *et al., Chem. Abs.*, 1988, **109**, 12825
6. Kondrikov, B. N. *et al., Chem. Abs.*, 1996, **125**, 172589

Polynitro derivatives of monocyclic aromatic systems (trinitrobenzene, trinitrotoluene, tetranitro-*N*-methylaniline, trinitrophenol, etc.) have long been used as explosives [1]. It has been found that a series of polynitroderivatives of biphenyl, diphenylmethane and 1,2-diphenylethylene (stilbene) are explosives liable to detonate on grinding or impact [2]. The same may be true of other polynitro derivatives of polycyclic systems not normally used as explosives (e.g. polynitro-fluorenones, –carbazoles, etc. Penta- and hexa-nitrobenzophenones are also high-energy explosives [3]. The thermal stability of 33 polynitroaromatics was studied by DTA [4]. Two empirical equations relating the heat of decomposition to the heat of detonation have been developed and used to calculate the heats of detonation for 47 polynitroaryl compounds [5].

The presence of 2 or more nitro groups (each with 2 oxygen atoms) on an aromatic nucleus often increases the reactivity of other substituents and the tendency towards explosive instability as oxygen balance is approached.

The effect of sulphuric acid, a likely impurity from the usual preparation, in increasing sensitivity to detonation and decomposition has been studied [6].

Individually indexed compounds are:

2-Acetylamino-3,5-dinitrothiophene, 2273
3-Amino-2,5-dinitrotoluene, 2779
2-Amino-4,6-dinitrophenol, 2271
* Ammonium 2,4,5-trinitroimidazolide, 1141
Ammonium 3-methyl-2,4,6-trinitrophenoxide, 2799
Ammonium picrate, 2315
2-Azido-3,5-dinitrofuran, 1380
2,2′-Azo-3,5-dinitropyridine, 3232
2-Benzylideneamino-4,6-dinitrophenol, 3594
Bis(2,4-dinitrophenyl) disulfide, 3443
Bis(2-nitrophenyl) disulfide, 3459
1,2-Bis(2-nitrophenyl)ethane, 3639
6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate, 2090
5-*tert*-Butyl-2,4,6-trinitro-1,3-xylene, 3526
Calcium picrate, 3424
2-Chloro-1,3-dinitro-5-trifluoromethylbenzene, 2633
1-Chloro-2,4-dinitrobenzene, 2091
6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2095
4-Chloro-2,6-dinitroaniline, 2147
2-Chloro-4,6-dinitroaniline, 2146
* Cobalt(II) picramate, 3454
Copper(II) 3,5-dinitroanthranilate, 3620
Copper(II) picrate, 3426
1,5-Dichloro-2,4-dinitrobenzene, 2070
1,5-Difluoro-2,4-dinitrobenzene, 2073
1,8-Dihydroxy-2,4,5,7-tetranitroanthraquinone, 3615
mixo-Dimethoxydinitroanthraquinone, 3694
4,6-Dinitro-1,3-benzenediol, 2191
* 5,6-Dinitro-2-dimethylaminopyrimidinone, 2351
3,5-Dinitro-2-methylbenzenediazonium-4-oxide, 2662
4,6-Dinitro-2-*sec*-butylphenol, 3300
3,5-Dinitro-2-toluamide, 2936
2,5-Dinitro-3-methylbenzoic acid, 2914
3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide, 2083
2,6-Dinitro-4-perchlorylphenol, 2094
3,5-Dinitro-6-methylbenzenediazonium-2-oxide, 2663
3,8-Dinitro-6-phenylphenanthridine, 3774
2,4-Dinitroaniline, 2270
1,4-Dinitrobenzene, 2189
1,3-Dinitrobenzene, 2188

1,2-Dinitrobenzene, 2187
1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3695
2,4-Dinitrobenzenediazonium hydrogen sulfate, 2199
* 2,4-Dinitrobenzenesulfenyl chloride, 2092
2,4-Dinitrobenzenesulfonyl chloride, 2093
4,6-Dinitrobenzofurazan *N*-oxide, 2082
2,6-Dinitrobenzyl bromide, 2668
1,5-Dinitronaphthalene, 3236
2,4-Dinitrophenol, 2190
2,4-Dinitrophenylhydrazinium perchlorate, 2344
O-(2,4-Dinitrophenyl)hydroxylamine, 2272
2,4-Dinitrotoluene, 2722
2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone, 3124
* 1-Fluoro-2,4-dinitrobenzene, 2101
2-Formylamino-3,5-dinitrothiophene, 1817
Hexanitrobenzene, 2628
4-Hydroxy-3,5-dinitrobenzenearsonic acid, 2213
2-Hydroxy-3,5-dinitropyridine, 1816
2-Iodo-3,5-dinitrobiphenyl, 3444
Lead 2,4,6-trinitroresorcinoxide, 2064
Lead 2-amino-4,6-dinitrophenoxide, 3462
Lead(II) picrate, 3430
Manganese picrate hydroxide, 3736
Mercury(II) picrate, 3427
3-Methyl-2,4,6-trinitrophenol, 2699
* 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate, 3758
Nickel 2,4-dinitrophenoxide hydroxide, 3739
Nickel picrate, 3429
4-Nitro-1-picryl-1,2,3-triazole, 2881
5-Nitro-2-picryltetrazole, 2634
1-Nitro-3-(2,4-dinitrophenyl)urea, 2701
4,6- or 5,6- or 5,7-Dinitro-1-picrylbenzotriazoles, 3432
Pentanitroaniline, 2086
Picric acid (2,4,6-Trinitrophenol), 2111
Picryl azide, 2085
1-Picryl-1,2,3-triazole, 2893
Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2249
Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2107
Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide, 2718
Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide, 2106
Silver 2-azido-4,6-dinitrophenoxide, 2068
Silver 3,5-dinitroanthranilate, 2638
Silver hexanitrodiphenylamide, 3423
Sodium 2,4-dinitrophenoxide, 2108
Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2104
Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide, 2946

Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide, 2193
N,2,4,6-Tetranitroaniline, 2116
2,3,4,6-Tetranitroaniline, 2115
N,2,3,5-Tetranitroaniline, 2114
1,3,6,8-Tetranitrocarbazole, 3436
1,3,6,8-Tetranitronaphthalene, 3231
N,2,4,6-Tetranitro-*N*-methylaniline, 2702
2,3,4,6-Tetranitrophenol, 2084
2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene, 3529
1,3,5-Triaminotrinitrobenzene, 2317
1,3,5-Trifluorotrinitrobenzene, 2050
2,4,6-Trinitrobenzoic acid, 2636
Trinitrophloroglucinol, 2113
Trinitroresorcinol, 2112
2,4,5-Trinitrotoluene, 2698
2,4,6-Trinitrotoluene, 2697
* 1,3,5-Tris(nitromethyl)benzene, 3139
Zinc picrate, 3431

See also NITROARYL COMPOUNDS

Bases, or Salts

Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389—390

In view of previous violent or explosive reactions, heating of di- and tri-nitroaryl compounds with alkalies, ammonia or *O*-ethylsulfuric acid salts in autoclaves should be avoided.

See Diethyl sulfate: 3,8-Dinitro-6-phenylphenanthridine
NITROAROMATIC—ALKALI HAZARDS

Potassium

Batz, M. L. *et al., J. Org. Chem.*, 1997, **62**, 2045

Potassium salts of the radical anions $\cdot N^+(O^-)_2Ar$ were prepared by treating nitroaromatics (nitrobenzene, o-, m-, & p-dinitrotoluene, 2,4,6-trinitrotoluene and trinitrobenzene with potassium in liquid ammonia and allowing the ammonia to evaporate. All were exceedingly sensitive, exploding on mild agitation of the flask onto which they had been deposited. They decomposed non-explosively in solution to give potassium nitrite and polymers (explosive in the case of TNT) Hydrogen cyanide was among the explosion products of those bearing ortho methyl groups. Presumably other alkali metals would form similar compounds.

POLYNITROAZOPYRIDINES $(O_2N)_2C_5H_2NN{=}NNC_5H_2(NO_2)_2$

Coburn, M. D., *J. Heterocyclic Chem.*, 1974, **11**, 1099—1100

Most of a series of azodinitropyridines and their hydrazine precursors were explosive, with a sensitivity comparable to that of RDX. Individual compounds are:

2,2′-Azo-3,5-dinitropyridine, 3232
2,6-Bis(2-picrylhydrazino)-3,5-dinitropyridine, 3729
2,6-Bis(picrylazo)-3,5-dinitropyridine, 3728

3,5-Dinitro-2-(picrylazo)pyridine, 3381
1-(3,5-Dinitro-2-pyridyl)-2-picrylhydrazine, 3383
See other HIGH-NITROGEN COMPOUNDS, POLYNITROARYL COMPOUNDS

POLYPEROXIDES

This group covers polymeric peroxides of indeterminate structure rather than polyfunctional macromolecules of known structure. These usually arise from autoxidation of susceptible monomers and are of very limited stability or explosive. Polymeric peroxide species described as hazardous include those derived from butadiene (highly explosive); isoprene, dimethylbutadiene (both strongly explosive); 1,5-*p*-menthadiene, 1,3-cyclohexadiene (both explode at 110°C); methyl methacrylate, vinyl acetate, styrene (all explode above 40°C); diethyl ether (extremely explosive even below 100°C); and 1,1-diphenylethylene, cyclopentadiene (both explode on heating).

Individually indexed entries are:

Poly(dimethylketene peroxide)
† Chloroethylene, 0726
† 1,3-Cyclohexadiene, 2354
† Cyclopentadiene, : Oxygen, 1851
† 1,1-Dichloroethylene, 0691
† Diethyl ether, 1691
2,4-Diethynyl-5-methylphenol, 3387
2,4-Diethynylphenol, 3238
2,3-Dimethyl-1,3-butadiene, 2401
6,6-Dimethylfulvene, 2962
1,1-Diphenylethylene, : Oxygen, 3635
Formaldehyde oxide polymer, 0418
† 1,5-Hexadien-3-yne, 2284
Hydrogen peroxide, : Poly(hydroxyacrylic acid lactone), etc., 4471
1,5-*p*-Menthadiene, 3332
† Methyl methacrylate, 1909
2-Methylacryaldehyde oxime, 1563
Oxygen (Gas), : Cyclooctatetraene, 4825
Oxygen (Gas), : Tetrafluoroethylene, 4825
Poly(1,3-butadiene peroxide), 1528
Poly(1,3-cyclohexadiene peroxide), 2380
Poly(ethylidene peroxide), 0831
* Poly(peroxyisobutyrolactone), 1531
Poly(styrene peroxide), 2952
Poly(vinyl acetate peroxide), 1534
Styrene, : Oxygen, 2940
† Tetrafluoroethylene, 0624
† Vinyl acetate, 1527
See Hydrogen peroxide: Ketones, Nitric acid

POLYPROPYLENE POWDER

Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 91

Polypropylene powder was being conveyed by suction through a duct system as an air dispersion, fines being retained in a filter trap upstream of the centrifugal fans. However, the relatively coarse filter allowed very fine powder to pass and it was eventually retained over a long period of time in a silencer on the fan outlet. The thickening deposit eventually self-heated and ignited, and the fire spread very rapidly in the air-stream. A second fire, also apparently with polypropylene powder, occurred in a flash-dryer and cyclone system. Washing of the dryer case with water had led to build-up of aggregated powder which had degraded, melted and ignited. Nitrogen purging has been introduced as a preventive measure.

See other SELF-HEATING AND IGNITION INCIDENTS

PRECIOUS METAL DERIVATIVES

Hasenpusch, W., *Chem.-Ztg.*, 1987, **111**, (2), 57—60

In a review of explosions involving derivatives of gold, silver and platinum, reactions of ammonia with gold and silver compounds, and of hydrogen in presence of platinum compounds are emphasised.

See also FULMINATING METALS, HEAVY METAL DERIVATIVES, HYDROGENATION CATALYSTS, HYDROGENATION INCIDENTS

PREPARATIVE HAZARDS

Preparative hazards have been noted for the following compounds:

4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3260
Acetyl chloride, 0731
Aluminium copper(I) sulfide, 0084
3-Amino-2,5-dinitrotoluene, 2779
4-Amino-4*H*-1,2,4-triazole, 0808
2-Amino-5-nitrothiazole, 1114
6-Aminopenicillanic acid *S*-oxide, 3005
Azidosilane, 4496
Aziridine, 0859
1,1′-Azo-[2-methyl-1,2-dicarbadecaborane(14)], 2620
2-Azoxyanisole, 3646
1,4-Benzenediol—oxygen complex, 2327
Benzeneperoxysulfonic acid, 2334
Benzeneseleninic acid, 2328
Benzeneseleninic anhydride, 3489
Benzenethiol, 2337
2,2′-Bi-1,3-dithiole, 2208
2,2′-Bipyridyl 1-oxide, 3252
1,2-Bis(2-nitrophenyl)ethane, 3639
Bis(cyclopentadienyl)lead, 3288
Bismuth trisulfide, 0234
Bis-*N*(imidosulfurdifluoridato)mercury, 4336

Hydrogen chloride, 3987
trans-4-Hydroperoxy-5-hydroxy-4-methylimidazolin-2-one, 1593
2-Hydroxy-2-methylglutaric acid, 2439
Hydroxyacetone, 1227
Indium bromide, 0288
Iodoethane, 0854
Iron(II) perchlorate, 4056
Isophthaloyl chloride, 2883
Magnesium, 4685
Mercury peroxide, 4601
4-Methoxy-3-nitrobenzoyl chloride, 2911
2-Methoxy-5-nitroaniline, 2798
4-Methoxybenzaldehyde, 2951
Methyl iminioformate chloride, 0893
3-Methyl-4-nitropyridine *N*-oxide, 2310
2-Methyl-5-nitrobenzenesulfonic acid, 2768
Methylborylene, 0424
Methylnitrothiophene, 1844
N-(3-Methylphenyl)-2-nitrobenzimidyl chloride, 3634
Methyltrifluoromethyltrichlorophosphorane, 0739
Molybdenum hexamethoxide, 2592
2-Nitroaniline, 2306
tert-Nitrobutane, 1655
Nitromesitylene, 3152
3-Nitrophthalic acid, 2901
3-Nitropropiophenone, 3135
N-Nitroso-6-hexanelactam, 2418
Nitrosylsulfuric acid, 4432
Nitroterephthalic acid, 2902
1,4-Octadecanolactone, 3767
1,4,8,11,15,18,22,25-Octamethyl-29*H*,31*H*-tetrabenzo[*b.g.l.q*]porphinato(2—)cobalt(II), 3904
Osmium(IV) oxide, 4827
4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2350
Pentaamminedinitrogenruthenium(II) salts, 4591
Pentafluoroorthoselenic acid, 4348
Pentanesulfonic acid, 2014
Perfluoro-*tert*-butanol, 1376
Peroxomonophosphoric acid, 4501
2-Phenyl-1,1-dimethylethyl hydroperoxide, 3326
N-Phenylhydroxylamine, 2349
Phenyllithium, 2252
Phenylsodium, 2280
Phosphoryl dichloride isocyanate, 0326
Phthalic anhydride, 2894
2-Piperidone, 1928

1,1,1-Tris(aminomethyl)ethane, 2038
1,1,1-Tris(bromomethyl)methane, 1545
Tris(cyclopentadienyl)cerium, 3676
Tris(hydroxymethyl)methylamine, 1725
Tungsten hexamethoxide, 2600
Tungsten tetrabromide oxide, 0293
Undecaamminetetraruthenium dodecaoxide, 4593
Xenon difluoride dioxide, 4316
Xenon tetrafluoride oxide, 4340
Zinc ethylsulfinate, 1705
See 1,2-DIOLS, 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE SALTS

PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

1. Grewer. T. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 657—664, Basle, SSCI, 1980
2. Klais, O. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C24—C34, Rugby, IChE, 1983
3. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1—9, Oxford, Pergamon, 1987
4. Watanabe, N. *et al., Chem. Abs.*, 1988, **108**, 207227

Equipment was developed to measure the maximum pressure and rate of pressure increase during exothermic decomposition, and the results serve as useful criteria to assess hazards. For each of the 6 compounds examined at a vessel loading of 0.1—0.2 g/cm^3, the starting temperature, max. pressure (bar) and max. rate of rise (bar/s), respectively, are given below.

Azobenzene, 340/ 13/ 6.5; azoformamide, 260/ 194/ 925; diketene, 125/ 140/ —; 4-nitroisopropylbenzene, 250/ > 182/ 830; 4-nitrophenol, 280/ > 199/ 1,030; 4-nitrosophenol, 120/ 23/ 5. It is concluded that the first and last compounds are of relatively low hazard [1]. Improved equipment has provided more accurate and detailed results for a further 7 compounds and has shown the effect of variations in the initial stage of decomposition on the final pressure attained, and of the increase in pressure causing a reduction in the rate of pressure rise. At 0.2 g/cm^3 loadings, comparable results are:—

A diazonium salt, 112/ 200/ 66; azoisobutyronitrile, 80/ 130/ 8,800; 1,3-diphenyltriazene, 140/ 95/ 420; 2-nitrobenzaldehyde, 200/ 945/ 8,700; 3-nitrobenzaldehyde, 190/ 830/ 4,100, 4-nitrobenzaldehyde, 200/ 960/ 4,700. Solids which deflagrate give substantially higher rates of pressure rise because the rate of pressure rise is not depressed by increase in pressure, e.g. ammonium dichromate, 227/ 510/ 68,000 [2].

Deflagration (progressive exothermic decomposition/combustion) may be rapid, as in propellant explosive compositions, or slow in non-explosive compounds. The high probability of deflagration in this latter type of industrially important materials, as indicated by the number of incidents involving the relatively few deflagrable non-explosives, has led to an investigation of deflagration and the pressure effects which accompany it. Deflagration rates (cm/min) measured by igniting the top of the material in a 5 cm diameter beaker and timing the downward progress were:- ammonium dichromate, 2.2; 1,3-diphenyltriazene, 2.0; hydroxylaminium sulfate, 5.6; 1-nitroso-2-naphthol, 0.74; 1-(2,4-dinitrophenylazo)-2-naphthol, 1.8; 4-nitrosophenol, 8; sodium 3-nitrobenzenesulfonate, 4.5 cm/min.

Most mononitroaryl compounds do not deflagrate, but mixed with an excess of sodium or potassium hydroxide they deflagrate readily. Some rates (cm/min) for such mixtures are:- 4-chloronitrobenzene + KOH (1:1.5 mol), 1.3; 4-nitrobenzoic acid + KOH (1:2 mol), 5.1; 4-nitrophenol + KOH (1:1.5 mol), 30; 2-nitrobenzaldehyde + active carbon (1.5:1 mol), 1.25 cm/min.

Pressure effects measured during deflagration with top-surface ignition in an unheated 200 ml autoclave, or during homogeneous decomposition (no ignition coil, autoclave heated slowly in an oven) led to some problems in interpreting the pressure-time curves in the latter case. Deflagration of 1,3-diphenyltriazene and of hydroxylaminium sulfate showed relatively slow rise of pressure (to 111, 250 bar in 600, 380 ms, respectively), while the results from homogeneous decomposition showed wider variations in the rate of pressure rise. Thus, 1,3-diphenyltriazene and 2-nitrobenzaldehyde showed slow rates of rise (to 132, 940 bar, in 600, 280 ms), while azoisobutyronitrile and ammonium dichromate showed fast rates (to 130, 480 bar during 30, 24 ms, respectively). Log-log plots of deflagration rates of pressure rise vs pressure show that for 1,3-diphenyltriazene, hydroxylaminium sulfate and 1-nitroso-2-naphthol, the rate is approximately proportional to pressure, while for ammonium dichromate it appears proportional to the square of the pressure [3].

In a study of deflagration of inorganic peroxide—combustible mixtures at compositions giving zero oxygen balance (and maximum rates of pressure rise), inorganic peroxides with cellulose give higher rates of rise than peroxoacids or hydrogen peroxide adducts (‘sodium percarbonate’), and some of these latter mixtures did not ignite. Mixtures of potassium chlorate with cellulose show high deflagration hazards and exhibit remarkable pressure increase effects [4].

Some incidents of this type may be found under:

Ammonium dichromate, 4240
Azoformamide, 0812
Azoisobutyronitrile, 3006
Azoisobutyronitrile, 3006
† *tert*-Butyl peroxybenzoate, 3397
4-Chloronitrobenzene, 2135
† 1,1-Difluoroethylene, 0696
† Diketene, 1437
1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3695
1,3-Diphenyltriazene, 3500
1,3-Diphenyltriazene, 3500
† Ethylene oxide, : Sucroglyceride, 0825
Hydroxylaminium sulfate, 4570
3-Methyl-4-nitrophenol, 2762
2-Nitrobenzaldehyde, 2682
2-Nitrobenzaldehyde, 2682
4-Nitrobenzaldehyde, 2684
4-Nitrobenzoic acid, : Potassium hydroxide, 2691
4-Nitroisopropylbenzene, 3151

4-Nitrophenol, 2260
4-Nitrophenol, : Potassium hydroxide, 2260
1-Nitroso-2-naphthol, 3244
4-Nitrosophenol, 2257
Sodium 3-nitrobenzenesulfonate, 2177
NITROBENZALDEHYDES
NITROBENZYL COMPOUNDS
PRESSURE RELIEF
ZINC BACITRACIN
See ISOXAZOLES

PRESSURE RELIEF

1. Huff, J. E., *Proc. Int. Symp. Prev. Major Chem. Accid.*, Washington, 1987, 4.43—4.67, New York, AIChE, 1987
2. Burgoyne, J. H., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 201—213, Oxford, Pergamon, 1987
3. Tippet, J. R. *et al., ibid.*, 358—361
4. Fauske, H. K., *ibid.*, 133—141
5. Bettis, R. J. *et al., ibid.*, 247—263
6. Fauske, H. K., *Plant/Oper. Progr.*, 1988, **7**(7), 3

The important role played by pressure relief arrangements to mitigate the effects of runaway exothermic reactions and to prevent catastrophic vessel failure is discussed. For full effectiveness, the pressure relief system must be included in the overall process design, and must be adequately sized to permit discharge of vessel contents at a safe pressure and to a safe location. Methods of achieving these objectives are presented [1], and problems associated with subsequent treatment of the materials from accidental discharges are discussed [2]. Methods of assessing relief requirements for reactive and non-reactive systems are considered, including runaway liquid phase reactions and fire-exposed liquid-filled storage vessels [4]. Special consideration is given to emergency releases involving 2-phase flow [4,5]. The scope of the AIChE design package of the Design Institute for Emergency Relief Systems (DIERS) has been extended to deal with both reactive and non-reactive mixtures being vented [6].

See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

PROTEINS

Pitts, J. E., *Nature*, 1992, **360**, 94

It is suggested that crystalline proteins are explosive, as evidenced by the easily induced shattering of the microcrystals currently available [1]. Except, possibly, where mercuric nitrate is involved, the editor suspects this of being implosive collapse of a metastable ordering of molecules.

See ORGANOMETALLIC NITRATES

PROPELLANTS

1. Gould, R. F., *Advanced Propellant Chemistry (ACS Monograph 54)*, Washington, Amer. Chem. Soc., 1966
2. Ullmann, 1993, *A22*, 185

Like other high energy materials deliberately made so (explosives and pyrotechnics) propellants in their proper use do not fall within the scope of this handbook. It is a field of considerable current development [2].

The above book [1] deals, in 26 chapters in 5 sections, with theoretical and practical aspects of the use and safe handling of powerful oxidants and their complementary reactive fuels. Materials include: nitrogen pentaoxide, perfluoroammonium ion and salts, nitronium tetrafluoroborate, hydrazinium mono- and di-perchlorates, nitronium perchlorate, tricyanomethyl compounds, difluoramine and its alkyl derivatives, oxygen difluoride, chlorine trifluoride, dinitrogen tetraoxide, bromine trifluoride nitrogen fluorides, and liquid ozone—fluorine system.

See also ROCKET PROPELLANTS

PYRAZOLONE DYESTUFF PREPARATION

Anon., *Loss Prev. Bull.*, 1979, (030), 160

A 300 g sample of the monoazo product of coupling a diazotised nitroaminophenol onto a pyrazolone exploded violently during vacuum drying at 110°C. Small samples filtered at pH 7.5 had been dried uneventfully, but the large batch had been at pH 8.8 (so may have contained some diazophenoxide). It was further found that parts of the oven were hotter by 20—30°C than the indicated temperature.

See ARENEDIAZONIUM OXIDES

PYROPHORIC ALLOYS

1. Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163—164
2. Kirk-Othmer, 1982, Vol. 19, 494

Alloys of reactive metals are often more pyrophoric than the parent metals. Examples are alloys of titanium with zirconium; thorium with copper, silver or gold; uranium with tin, lead or gold; magnesium with aluminium; hafnium with iron [1]. Cerium amalgams and thorium—silver alloys are spontaneously flammable when dry [2].

Individually indexed alloys are:
Aluminium—lanthanum—nickel alloy, 0080
Cerium: Alone, or Metals, 3955
Lead—zirconium alloys, 4878
Silver—thorium alloy, 0004
Zinc amalgam, 4596

See other PYROPHORIC MATERIALS

PYROPHORIC CATALYSTS

1. *Laboratory Handling of Metal Catalysts*, in *Chem. Safety*, 1949, (2), 5
2. *Catalyst Handbook*, 180—181, London, Wolfe, 1970

A proposed Code of Practice for laboratory handling of potentially pyrophoric catalysts includes: storage in tightly closed containers; extreme care in transfer operations, with provision for immediate cleaning up of spills and copious water flushing; avoidance of air-drying during filtration, and storage of residues under water; use of water-flush in case of ignition [1]. The later reference details precautions to prevent fires in catalysts discharged from industrial reactors [2].

Some examples are:

Dodecacarbonyltetracobalt, 3414

Nickel, : Magnesium silicate, 4814

See COPPER CHROMITE CATALYST HYDROGENATION CATALYSTS

PYROPHORIC IRON—SULFUR COMPOUNDS

1. Schultze, R. *et al., Arbeitsschutz*, 1964, 194—196
2. Dodonov, Ya. Ya. *et al., Chem. Abs.*, 1964, **60**, 5058h—5059a
3. Anon., *Loss. Prev. Bull.*, 1977, (012), 1—6
4. Kletz, T. A., *Loss Prev. Bull.*, 1982, (048), 19—20
5. Bitay-Fulop, M. *et al., Chem. Abs.*, 1979, **91**, 94069
6. Gendel, G. L. *et al., Chem. Abs.*, 1982, **96**, 183813
7. Kyazimov, A. M. *et al., Chem. Abs.*, 1982, **97**, 186029
8. Hempel, D. *et al., Chem. Tech.* (Leipzig), 1983, **35**, 525—529
9. Walker, R. *et al., Surf. Coating Technol.*, 1987, **31**, 163—197
10. Kostur, P. *et al., Chem. Abs.*, 1988, **108** 97651
11. Sahdev, M., www.chemresourcees.com/ironfires.shtml, 2002
12. Roling, P.V. *et al.*, US Pat., 6,328,943, 2001

Iron(III) salts and thiols in alcoholic solution interact to produce highly pyrophoric mixtures containing iron alkylsulfides, iron oxide, hydrates, sulfides and sulfur. Effects of variation in reaction conditions and structure of thiols upon pyrophoricity were examined. Treatment of the pyrophoric mixtures with nitrogen oxide to form nitrosyl complexes effectively deactivates them [1]. Laboratory treatment of hydrated iron oxides with hydrogen sulfide simulated the production of pyrophoric iron sulfides which frequently cause fires in petroleum refining operations. Presence of gasoline during sulfide preparation gave pyrophoric materials which retained their activity longer than when gasoline was absent [2]. Several petroleum refinery fires and incidents are detailed [3]. In the investigation of a petroleum storage tank explosion in 1936, it was noticed that disturbing the sulfide scale in a tank gave several sparks, one of which, trapped in the scale caused incandescence of about 5 seconds duration. This type of occurrence may have been the original ignition source [4]. An apparatus and method for assessing the pyrophoric activity of these deposits is described [5], and their laboratory preparation in presence of amines or polyethylene glycols has been studied [6]. There have been studies of the possibility of suppression of spontaneous ignition of Fe—S deposits by corrosion inhibitors [7] or by other means [8,12]. The factors affecting the type of pyrophoric deposit produced from rust and petroleum-derived hydrogen sulfide are discussed [9]. Measures to inactivate such deposits call for their slow oxidation with steam—air, or dilute oxygen—inert gas mixtures [10]. A more recent paper on this problem and applicable chemical oxidants for plant treatment has appeared on the Web [11].

Some examples are:

2-Hydroxyethylamine, : Carbon dioxide, etc., 0939
Iron disulfide, 4395
Iron(II) sulfide, 4394
Iron(III) sulfide, 4398
Phthalic anhydride, 2894

PYROPHORIC MATERIALS

1. Kayser, E. G. *et al., Spontaneously Combustible Solids* — Literature Survey, Rept. 75-159, US Naval Weapons Center, (USNTIS AD-A019919), 1975
2. Carson, P. A., Mumford, C. J., *Loss Prev. Bull.* 1993, (109), 11; *ibid*., (110), 9

Existing information on solids spontaneously combustible in contact with air or water has been reviewed, with 145 references. Data relevant to the causes and prevention of spontaneous ignition are included, as well as the application of mathematical treatments to the problem, and available testing methods for assessing relevant factors in natural and manufactured products are discussed [1]. A two part review of pyrophoric materials and precautions in handling them is given [2].

Separate treatment is given for the relevant groups below:

Individually indexed compounds are:

Bis(acrylonitrile)nickel(0), 2305
* 1,2-Bis(dichlorophosphino)ethane, 0793
Bis(trimethylsilyl) phosphonite, 2607
Bromodimethylborane, 0883
Calcium silicide, 3937
Cerium trisulfide, 3961
Chromium(II) acetate, 1489
Chromium(II) oxide, 4235
Cobalt(II) sulfide, 4212
Cobalt(III) nitride, 4208
Dicobalt boride, 0128
Dimethyl ethanephosphonite, 1726
Europium(II) sulfide, 4287
2-Furaldehyde, 1830
Indium(II) oxide, 4636
Iron(II) chelate of bis-*N,N′*-(2-pentanon-4-ylidene)-1,3-diamino-2-hydroxypropane, 3610
Iron(II) hydroxide, 4386
Iron(II) maleate, 1389
Lead pentaphosphide, 4875
Lithium diethylamide, 1680
Lithium—tin alloys, 4677
Magnesium hydride, 4457
Manganese(II) *N,N*-diethyldithiocarbamate, 3352

Manganese(II) sulfide, 4701
5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole, 2449
Molybdenum(IV) oxide, 4711
Osmium(IV) oxide, 4827
† Phosphorus, 4868
Plutonium bismuthide, 0231
Poly(cyclopentadienyltitanium dichloride), 1837
* Poly(difluorosilylene), 4324
Potassium antimonide, 4668
Potassium *tert*-butoxide, 1645
Potassium cyclopentadienide, 1840
Potassium diethylamide, 1679
Potassium octacyanodicobaltate(8—), 2875
Potassium—sodium alloy, 4641
Silicon oxide, 4822
* Silver isophthalate, 2882
Sodium diethylamide, 1682
Sodium germanide, 4412
Thorium dihydride, 4483
* Thorium oxide sulfide, 4820
Titanium dibromide, 0283
Titanium dihydride, 4484
Titanium diiodide, 4625
Titanium trichloride, 4152
* Tricyclopentadienyluranium tetrahydroaluminate, 3681
Tris(2,2′-bipyridine)chromium(0), 3869
Uranium carbide, 0559
Uranium(III) nitride, 4727
Uranium(IV) oxide, 4837
Zinc, 4921
Zirconium dibromide, 0284
* Zirconium oxide sulfide, 4821

ALKYLALUMINIUM DERIVATIVES
ALKYLBORANES
ALKYLHALOBORANES
ALKYLHALOPHOSPHINES
ALKYLHALOSILANES
ALKYLMETALS
ALKYLNON-METAL HYDRIDES
ALKYLPHOSPHINES
ALKYLSILANES
ARYLMETALS
BORANES
CARBONYLMETALS
COMPLEX ACETYLIDES
COMPLEX HYDRIDES

HALOACETYLENE DERIVATIVES
HEXAMETHYLNITRATODIALUMINATE SALTS
METAL HYDRIDES
NON-METAL HYDRIDES
ORGANOMETALLICS
PYROPHORIC ALLOYS
PYROPHORIC CATALYSTS
PYROPHORIC IRON—SULFUR COMPOUNDS
PYROPHORIC METALS
See also METAL DUSTS (reference 3), THORIUM FURNACE RESIDUES

PYROPHORIC METALS

1. Feitknecht, W., *Conf. on Finely Divided Solids*, Commis l'Én. Atom., Saclay, 27—29 Sept., 1967
2. Peer, L. H. *et al., Mill & Factory*, 1959, **65**(2), 79
3. Anon., *Chem. Eng. News*, 1952, **30**, 3210
4. Breidenfeld, J., *Metall.*, 1954, **8**, 94—97
5. Koelman, B. *et al., Metal Progress*, 1953, **63**(2), 77—79
6. Popov, E. L. *et al., Chem. Abs.*, 1975, **83**, 135768
7. Evans, J. D. *et al., Powder Metall.*, 1976, **19**, 17—21
8. Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 157—172
9. Nedin, V. V.; Kostina, E. S., *Chem. Abs.*, 1977, **86**, 157758, 157759
10. Klabunde, K. J. *et al., Inorg. Synth.*, 1979, **19**, 59—86

Finely divided metal powders develop pyrophoricity when a critical specific surface area is exceeded; this is ascribed to high heat of oxide formation on exposure to air. Safe handling is possible in relatively low concentrations of oxygen in an inert gas [1]. Safe handling, storage, disposal, and fire fighting techniques for hafnium, titanium, uranium and thorium, and hazards of machining the 2 latter metals are discussed [2]. Dry finely divided tantalum, thorium, titanium, zirconium metals, or titanium—nickel, zirconium—copper alloys are not normally shock-sensitive. However, if they are enclosed in glass bottles which break on impact, ignition will occur. Storage of these materials moist and in metal containers is recommended [3].

Heat of combustion, thermal conductivity, surface area and other factors influencing pyrophoricity of aluminium, cobalt, iron, magnesium and nickel powders are discussed [4]. The relationship between heat of formation of the metal oxide and particle size of metals in pyrophoric powders is discussed for several metals and alloys including copper [5]. Further work on the relationship of surface area and ignition temperature for copper, manganese and silicon [6], and for iron and titanium [7] was reported. The latter also includes a simple calorimetric test to determine ignition temperature.

In a literature review with 115 references, factors influencing the pyrophoricity of metals are identified as particle size, presence of moisture, nature of the surface of the particle, heat of formation of the oxide or nitride, mass, hydrogen content, stress, purity and presence of oxide, among others. Static charge hazards, fire and explosion incidents, handling procedures and transport considerations are also discussed. References are given to reviews of incidents involving barium, beryllium, magnesium, paper, plutonium, polypropylene, thorium, titanium, zinc-rich coatings and zirconium [8]. Equations to calculate the lower ignition limits for explosive suspensions in air of aluminium, iron, magnesium, manganese, tantalum, tin and titanium powders have been derived. Results for the latter agree well with experimental findings [9]. The reaction residues from various metal atom syntheses (involving vacuum evaporation of cobalt, copper, chromium, iron, magnesium, manganese, nickel, palladium, platinum, tungsten, vanadium or zinc, and co-deposition with a ligand) are often pyrophoric, and suitable precautions are detailed [10].

Individually indexed pyrophoric metals are:
Barium, 0200
Cadmium, 3943
Caesium, 4248
Calcium, 3916
Cerium, 3955
Chromium, 4216
Cobalt, 4193
Europium, 4286
Hafnium, 4594
Iridium, 4638
Iron, 4382
Lead, 4876
Manganese, 4695
Nickel, 4814
Palladium, 4879
Platinum, 4881
Plutonium, 4882
Rhodium, 4886
Rubidium, 4883
Strontium, 4907
Tantalum, 4908
Technetium, 4909
Thorium, 4911
Titanium, 4913
Tungsten, 4919
Uranium, 4917
Vanadium, 4918
Zinc, 4921
Zirconium, 4922
See Aluminium amalgam, Bismuth plutonide

PYROTECHNICS

1. Hardt, A. P., in Kirk-Othmer, 1982, Vol. 19, 484—499
2. Wharton, R. K., *Proc. Int. Pyrotech. Semin.*, 1991, **16**, 514
3. Ullmann, 1993, *A22*, 437
4. Kirk-Othmer, 1996, Vol. 20, 680

5. Jennings-White, C. *et al., J. Pyrotech.*, 1995, (2), 72
6. Hatanaka, S. *et al., Kayaku Gakkaishi*, 1997, **57**(5), 213 & 220

With the possible exception of delay fuses, any pyrotechnic mixture represents a hazard worthy of report. Although the cause of frequent accidents reviewed in [2], compositions intended to explode or deflagrate are generally outside the field of this work and few are listed. Numerous reviews and specialist texts exist and hundreds of patents appear yearly. The account [1] of the theory and practice of pyrotechnics contains much useful information on the performance and potential hazards of a great variety of oxidant—fuel combinations which burn very rapidly or explosively. Safety measures are found in [2]. Other reviews written from a functional viewpoint are found in [3] and [4]. Some hazardously incompatible pyrotechnic mixes are reported [5]. Detonability of pyrotechnic compositions has been studied. Whistles and chlorate or perchlorate & aluminium containing noise compositions often show detonability. Most others do not [6].

Water

Gu, W. *et al., Kayaku Gakkaishi*, 1996, **57**(5), 204

There is some risk of pyrotechnic mixtures containing powders of magnesium, aluminium, their alloy, or zinc, igniting from exothermic reactions of the metal in damp storage. Some study of inhibitors is undertaken. Titanium seems relatively inactive.

QUALITATIVE ANALYSIS

See Lead(II) picrate

See also Nitric acid: Metal salicylates

QUATERNARY OXIDANTS

(QUATERNARY PERMANGANATES)

1. Author's comments
2. Leddy, B. P. *et al., Tetrahedron Lett.*, 1980, **21**, 2261—2262
3. Karaman, H. *et al., J. Org. Chem.*, 1984, **49**, 4509—4516
4. Bretherick, L., *J. Chem. Educ.*, 1987, **64**(2), A42—A44

In an attempt to find new oxidants which will function homogeneously in organic substrate/solvent systems, many salts with quaternary organic cations and oxidising anions have been prepared. There is however an intrinsic problem associated with this approach in that the compounds so prepared are effectively complete fuel—oxidant systems at the molecular level, with the oxidising anions juxtaposed in the crystal lattice with the organic cations. There have been a number of instances of unheralded and violent decomposition with this type of compound, which taken together suggest that considerable caution is necessary in preparing, storing and using these potentially hazardous salts [1].

Of a series of quaternary permanganate salts examined as organic oxidants, those of the 'unsaturated' cations benzyltrimethylammonium, benzyltriethylammonium, methyltriphenylphosphonium, ethylenebis(triphenylphosphonium) and hexadecylpyridinium all decomposed explosively at ~80—90°C, and of tetraphenylarsonium at 120—130°C. The permanganate salts of the 'saturated' cations tetramethylammonium, tetraethylammonium and hexadecyltrimethylammonium decomposed passively at 80—100°C, and were approximately as effective oxidants as their explosive counterparts. The latter could be considerably stabilised for use by adsorption on alumina [2]. General methods for the preparation and purification of a series of 16 quaternary ammonium permanganates and of 13 quaternary phosphonium permanganates have been developed, and the properties, decomposition temperatures and solubilities in 4 organic solvents and in water are tabulated. Examination of the thermal instability and mode of decomposition of several of the salts leads to the conclusion that thermal stability of these salts is a matter of concern, and that the salts should be held only in small quantity and in cold storage at all times, and that care should be exercised whenever they are handled and transferred from one container to another. Benzyltriethylammonium permanganate appears to be the best choice for long term storage stability, with dichloromethane as an appropriate reaction solvent [3]. Possible structures for more stable quaternary oxidant salts are discussed [4].

Individually indexed compounds are:
Benzyltriethylammonium permanganate, 3611
Benzyltrimethylammonium permanganate, 3336
1,2-Bis(triphenylphosphonio)ethane permanganate, 3893
N-Hexadecylpyridinium permanganate, 3821
Methyltriphenylphosphonium permanganate, 3778
Tetrabutylammonium hydrogen monoperoxysulfate, 3726
Tetrabutylammonium permanganate, 3723
Tetraethylammonium perchlorate, 3082
Tetraethylammonium periodate, 3084
Tetramethylammonium ozonate, 1747
Tetramethylammonium pentaperoxodichromate, 3097
Tetramethylammonium periodate, 1743
Tetramethylammonium superoxide, 1745
Tetraphenylarsonium permanganate, 3842

PERCHLORATE SALTS OF NITROGENOUS BASES
See DICHROMATE SALTS OF NITROGENOUS BASES
See other OXOSALTS OF NITROGENOUS BASES

RADICAL INITIATORS

1. Whitmore, M. W. *et al., J. Loss Prev.*, 1993, **6**(2), 95
2. Bravo, S. *et al., Chem. Eng. Progress*, 1994, **90**(7), 62
3. Anon., personal communication, 1999
4. Yoshida, T. *et al., Safety of Reactive Chemicals and Pyrotechnics*, Amsterdam, Elsevier, 1995

Apart from their ability to promote reactions beyond control, when used in excess, many polymerisation ‘catalysts’ of this class are dangerously unstable, to weakly explosive, in their own right. A table of accelerating reaction temperatures, determined by various methods, is given for many of these. The two main classes, azoorganics and peroxides, are likely to destabilise each other and should not be stored together in bulk [1]. A paper treats of safe handling of radical initiators and other polymerisation catalysts [2]. In the aftermath of an incident on a speciality polymer plant, where many different monomers and initiation systems were employed, it came to light that sparks were frequently observed when sweeping the floor. It was recommended that the floor be cleaned wet in future [3]. Explosivity tests on common initiators are reported in [4].

See Ammonium peroxodisulfate

See also ACCELERATING RATE CALORIMETRY, SELF-ACCELERATING DECOMPOSITION TEMPERATURE

RANEY ALLOYS

Aluminium—nickel alloys, 0055

See Aluminium—cobalt alloy

See also HYDROGENATION CATALYSTS

REACTION SAFETY CALORIMETRY

1. *Proc. Int. Symp. Prev. Risks Chem. Ind.*, Heidelberg, ISSA, 1976
2. Hub, L., *Proc. 6th Symp. Chem. Proc. Haz. Ref. Plant Des.*, 39—46, Rugby, IChE, 1977
3. *See entry* HEAT FLOW CALORIMETRY
4. Grob, B. *et al., Thermochim. Acta*, 1987, **114**, 83—90
5. Singh, J., *Process Safety Progress*, 1997, **16**(1), 43.
6. Burke, P. E., Spec. Publ. - R. Soc. Chem., 1997, 195(Pilot Plants and Scale-up of Chemical Processes).
7. le Parlouer, P. *et al., Proc. 28th NATAS Annu. Conf. Therm. Anal. Appl.*, 2000, 340
8. Editor's comment, 2005

One of the sessions of the Symposium was largely devoted to presentation and discussion on the use of various experimental calorimetric methods for use in assessing possible hazards in chemical processing operations. The methods described covered a wide range of sample sizes and degrees of complexity:

Grewer, T. Adiabatic small-scale reaction test in Dewar, simple to operate.

Janin, R. Measurements of heat release by DSC and of pressure development in sealed microcapsules.

Lemke, D. Heat accumulation tests of medium scale samples of thermally unstable technical materials in adiabatic storage.

Schleicher, K. Survey of general hazard testing methods.

Eigenmann, K. Use of micromethods in DTA, DSC.

Hub, L. Medium-small-scale safety calorimeter, usable under isothermal, quasi-isothermal or adiabatic conditions.

Regenass, W. Medium-scale heat flow calorimeter for measurement of heat release and cooling requirements under realistic reaction conditions.

Schofield, F. Use of a range of tests to determine detonation capability, localised thermal decomposition, thermal stability of reaction masses and effects of prolonged storage; translation of these results to industrial-scale processing operations.

Berthold, W. Use of adiabatic autoclave to simulate possibilty of thermal explosion in large containers of reactive materials [1].

Use of medium-scale heat flow calorimeter for separate measurement of reaction heat removed via reaction vessel walls and via reflux condenser system, under fully realistic processing conditions, with data processing of the results is reported [2]. More details are given elsewhere [3]. A new computer controlled reaction calorimeter is described which has been developed for the laboratory study of all process aspects on 0.5—2 l scale. It provides precise data on reaction kinetics, thermochemistry, and heat transfer. Its features are exemplified by a study of the (exothermic) nitration of benzaldehyde [4]. A more recent review of reaction safety calorimetry gives some comment on possibly deceptive results [5]. A further discussion of heat flow calorimetry in safe scale-up is found in [6]. A differential reaction calorimeter which is easy for chemists to use and employs on ten gram quantities of reagents has been described [7]. In the editor's experience, there can be problems in that manufacturing chemists often work in multiphase systems. This in turn demands good agitation, which, especially when packed with additional instrumentation, many reaction calorimeters do not provide. It can also affect the determination of heat capacity, which forms part of the in-test calibration of a trial, the capacity of a saturated solution over a crystalline reagent or product may be much different to that of any solution which forms at higher temperatures [8].

See CHEMICAL STABILITY/REACTIVITY ASSESSMENT

See also ACCELERATING RATE CALORIMETRY, ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY, DIFFERENTIAL SCANNING CALORIMETRY (DSC)

REACTION SIMULATION

Wright, A. *et al., Chem. & Ind.*, 1988, 114—118

A reaction simulation program, REACTION, which will run on a personal computer, and which is specifically adapted for the non-steady states prevailing in batch reactions, is described and illustrated by a typical reaction model. Among uses of the program for rapidly studying reaction engineering, process optimisation, control systems, scale-up and staff training requirements, are included thermal stability and process safety studies.

REACTIVE METALS

Stout, E. L., *Los Alamos Sci. Lab. Rept.*, Washington, USAEC, 1957; *Chem. Eng. News*, 1958, **36**(8), 64—65

Safety considerations in handling plutonium, uranium, thorium, alkali metals, titanium, magnesium, and calcium are discussed.

REDOX COMPOUNDS

Compounds which contain both oxidising and reducing functions in close proximity on a molecular basis tend towards explosive instability, and usually with low energy of activation. Relevant types are salts of reducing bases with oxidising acids, and metal oxosalts with coordinated nitrogenous reducants.

and the individually indexed compounds:

(Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2610

Bis(hydrazine)diperchloratochromium(III) perchlorate, 4122

* Borane—bis(2,2-dinitropropylhydrazine), 0137
Copper(I) perchlorate, 4052
Copper(II) phosphinate, 4266
Diamminenitratocobalt(II) nitrate, 4196
Hydrazinium chlorate, 4004
Hydrazinium chlorite, 4002
Hydrazinium nitrate, 4544
Hydrazinium perchlorate, 4005
Hydroxylaminium nitrate, 4519
Hydroxylaminium perchlorate, 3999
Indium(I) perchlorate, 4008
Iron(II) perchlorate, 4056
Iron(III) phosphinate, 4388
Lead(II) nitrate phosphinate, 4462
Manganese(II) chlorate, 4081
Manganese(II) perchlorate, 1779
Mercury(I) chlorite, 4074
Pentaamminephosphinatochromium(III) perchlorate, 4047
Pentaamminephosphinatocobalt(III) perchlorate, 4044
Pentaamminethiocyanatoruthenium(III) perchlorate, 0517
Peroxyformic acid, 0419
* Phosphonium perchlorate, 4000
Potassium cyanide—potassium nitrite, 0524
* Potassium pentacyanodiperoxochromate(5—), 1804
Potassium tricyanodiperoxochromate(3—), 1041
Tetrahydroxotritin(2+) nitrate, 4520
* Tetrakis(hydroxymethyl)phosphonium nitrate, 1748
Tin(II) nitrate, 4745
Tin(II) perchlorate, 4103
Trihydrazinealuminium perchlorate, 0064
Trimethylhydroxylammonium perchlorate, 1319
* Triphenylphosphine oxide hydrogen peroxidate, 3749
CHLORITE SALTS
PERCHLORATE SALTS OF NITROGENOUS BASES
See AMMINEMETAL OXOSALTS, OXOSALTS OF NITROGENOUS BASES
See also DRUMS, OXYGEN BALANCE

REDOX REACTIONS

Incidents involving interaction of active oxidants and reducing agents, either by design or accident, are usually extremely energetic, and examples of such redox reactions will be found under the entries:

* (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2610
* Calcium hypochlorite, : Acetic acid, Potassium cyanide, 3918
Cerium, : Water, 3955
Copper(II) nitrate, : Ammonium hexacyanoferrate(II), 4273

Dibenzoyl peroxide, : Lithium tetrahydroaluminate, 3632
N,N-Dimethyl-4-nitrosoaniline, : Acetic anhydride, Acetic acid, 2975
Dinitrogen oxide, 4739
Dinitrogen tetraoxide, : Formaldehyde, 4720
Ethyl hydroperoxide, : Hydriodic acid, 0921
Hydrogen peroxide, : Lithium tetrahydroaluminate, 4471
Hydroxylamine, 4493
Hydroxylamine, : Oxidants, 4493
Lead(IV) oxide, : Carbon black, Chlorinated paraffin, Manganese(IV) oxide, 4828
Magnesium nitrate, : Tin(II) fluoride, 4688
Manganese(IV) oxide, : Calcium hydride, 4700
Molybdenum(VI) oxide, : Graphite, 4712
Nitric acid, : Formaldehyde, 4430
Nitric acid, : Formic acid, 4430
Nitric acid, : Formic acid, Urea, 4430
Nitric acid, : Metal thiocyanate, 4430
Oxalic acid, : Urea, 0721
Ozone, : Acetylene, 4840
Perchloric acid, : Iron(II) sulfate, 3992
Perchloric acid, : Sodium phosphinate, 3992
Perchloric acid, : Zinc phosphide, 3992
α-Phenylazobenzyl hydroperoxide, : Phenylhydrazine, 3603
Phosphinic acid, : Mercury(II) oxide, 4498
Phosphonium iodide, : Oxidants, 4510
Potassium nitrate, : Reducants, 4645
Potassium phosphinate, : Air, or Nitric acid, 4453
Silver nitrate, : Magnesium, Water, 0022
Sodium chlorite, : Phosphorus, 4032
Sodium hypochlorite, : Formic acid, 4031
Sodium nitrate, : Arsenic trioxide, Iron(II) sulfate, 4716
Sodium nitrate, : Sodium phosphinate, 4716
Sodium nitrate, : Sodium thiosulfate, 4716
Sodium nitrate, : Tris(cyclopentadienyl)cerium, 4716
Sodium nitrite, : Potassium thiocyante, 4715
Sodium nitrite, : Sodium disulfite, 4715
Sodium nitrite, : Sodium thiocyanate, 4715
Sodium thiosulfate, : Sodium nitrite, 4798
1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, : Lithium tetrahydroaluminate, 3306
Thallium(III) nitrate, 4757
METAL NITRATES: Esters, or Phosphorus, or Tin(II) chloride
METAL NITRATES: Metal phosphinates
METAL PERCHLORATES: Calcium hydride
PERCHLORATES: Reducants
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

REDUCANTS

Most of the compounds showing powerful reducing action have been listed separately under the group headings below:

The remaining individually indexed compounds are:

Aluminium, 0048
Ammonium phosphinate, 4549
Barium phosphinate, 0210
† Benzaldehyde, 2727
1,4-Benzenediol, 2326
* Bis(hydrazine)tin(II) chloride, 4064
Calcium acetylide, 0582
Calcium phosphinate, 3925
Chromium(II) chloride, 4046
Chromium(II) oxide, 4235
Chromium(II) sulfate, 4238
Copper(I) bromide, 0264
Diacetatotetraaquocobalt, 1774
Diisobutylaluminium hydride, 3076
† 1,2-Dimethylhydrazine, 0951
1,2-Diphenylhydrazine, 3511
Dipotassium phosphinate, 4425
† Ethanedial, 0719
† Formaldehyde, 0415
Formic acid, 0417
Gallium(I) oxide, 4405
Glucose, 2513
† Hydrazine, 4515
Hydroxylamine, 4493
Hydroxylaminium phosphinate, 4550
Hyponitrous acid, 4464
Iron(II) chloride, 4055
Iron(II) hydroxide, 4386
Iron(II) sulfate, 4393
Lead(II) phosphinate, 4526
Lead(II) phosphite, 4530
Lithium dithionite, 4682
Magnesium, 4685
Magnesium phosphinate, 4512
Manganese(II) phosphinate, 4514
† Methylhydrazine, 0500
Phenylhydrazine, 2366
Phosphinic acid, 4498
Phosphonic acid, 4499
Phosphonium iodide, 4510
Potassium, 4640
Potassium hypoborate, 0163

Potassium phosphinate, 4453
Sodium disulfite, 4802
Sodium dithionite, 4801
Sodium hydride, 4438
Sodium hypoborate, 0164
Sodium phosphinate, 4467
Sodium thiosulfate, 4798
Sulfur dioxide, 4831
Tetraphosphorus hexaoxide, 4861
Tin(II) chloride, 4064
Tin(II) fluoride, 4325
Titanium trichloride, 4152
Titanium(II) chloride, 4111
Tungsten dichloride, 4113
Vanadium dichloride, 4112
Vanadium trichloride, 4153
Zinc, 4921
Zirconium trichloride, 4154
Zirconium(II) chloride, 4115

COMPLEX HYDRIDES
METAL ACETYLIDES
METAL HYDRIDES

REFRACTORY POWDERS

Krivtsov, V. A. *et al., Chem. Abs.*, 1979, **90**, 125991

Of a series of powdered refractory compounds examined, only lanthanum hexaboride, hafnium carbide, titanium carbide, zirconium carbide, magnesium nitride, zirconium nitride and tin(II) sulfide were dust explosion hazardous, the 2 latter being comparable with metal dusts. Individual entries are:

Hafnium carbide, 0518
Lanthanum hexaboride, 0193
Magnesium nitride, 4693
Tin(II) sulfide, 4894
Titanium carbide, 0558
Zirconium carbide, 0562
Zirconium nitride, 4728

REFRIGERATORS

1. Hasenpusch, W., *CLB Chem. Labor, Biotech.*, 1995, 46(5), 212, 214
2. Lindborg, A., *DKV – Tagungsbericht*, 2002, 30th(Vol 2 Pt 1) 301,

Explosions in laboratory refrigerators are fairly common, often because volatile solvents such as ether are below their upper flammable limit in a refrigerator, but not in a solvent cabinet. The domestic refrigerators usually employed are far from flame-proofed. The review discusses causes and recommends precautions [1]. Another paper discusses explosions caused by refrigerant gas-leaks [2].

See also FLAMMABILITY, FLASH POINTS

REPAIR AND MAINTENANCE

1. *Management of Change in Chemical Plants*, Sanders, R. E., Oxford, Butterworth-Heinemann, 1993.
2. Anon., *Loss Prev. Bull.*, 1992, **107**, 17

These activities may introduce many hazards, such as contaminants, materials of repair corrodible, combustible or catalytic in the given environment, blocked vents, open valves etc. into the restarted plant, while shutdown and startup are, in any event, the most dangerous periods. Many examples of reactive hazards thus introduced are to be found in [1]. Mutatis mutandis, this is also true of the laboratory; this Handbook contains many incidents consequent upon stopping a reaction and/or its agitation to sample, change cooling bath, etc.

If the shutdown for repair is enforced by equipment failure, and thus abnormal, risks are greater; an explosion and fire resulted from failure of the airblower in an operating cracking catalyst regeneration unit, which was then steamed through, vented to the air and allowed to cool for two days prior to opening to replace the catalyst, whereupon the mishap occurred. Investigation suggested that the steam had formed water gas and light hydrocarbons by reaction with coke on the catalyst, and that these had not vented, nor had air penetrated enough to burn off combustibles from the probably still hot catalyst [2].

See CATALYTIC IMPURITY INCIDENTS

ROCKET PROPELLANTS

1. Kirk-Othmer, 1965, Vol. 8, 659
2. Urbanski, 1967, Vol. 3, 291
3. *ACS 88*, 1969

All of the theoretically possible high-energy (and potentially hazardous) oxidant—fuel systems have been considered for use, and many have been evaluated, in rocket propulsion systems (with apparently the sole exception of the most potent combination, liquid ozone—liquid acetylene). Some of the materials which have been examined are listed below, and it is apparent that any preparative reactions deliberately involving oxidant—fuel pairs must be conducted under controlled conditions with appropriate precautions to limit the rate of energy release.

Many of the possible combinations below are hypergolic (will ignite on contact) or can be made so with additives. A few single compounds have been examined as monopropellants (alkyl nitrates, ethylene oxide, hydrazine, hydrogen peroxide), the two latter being catalytically decomposed in this application. Solid propellant mixtures, which are of necessity long-term storage stable, often contain ammonium or hydrazinium perchlorates as oxidants. The hazardous aspects of rocket propellant technology have been surveyed [3].

OXIDANTS	FUELS
Chlorine trifluoride	Alcohols
Dinitrogen tetraoxide	Amines
Fluorine	Ammonia
Fluorine oxides	Beryllium alkyls
Halogen fluorides	Boranes
Methyl nitrate	Dicyanogen
Nitric acid	Hydrazines
Nitrogen trifluoride	Hydrocarbons
Oxygen	Hydrogen
Ozone	Metal hydrides
Perchloric acid	Nitroalkanes
Perchloryl fluoride	Powdered metals
Tetrafluorohydrazine	Silanes
Tetranitromethane	Thiols

See also PROPELLANTS

ROSIN **(complex mixture, mainly resin acids)**

Dry finely divided rosin is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

ROSINATED PIGMENTS

Twitchett, H. J., *Chem. Brit.*, 1977, **13**, 437

These products, usually calcium or barium 'lakes' of acid azo-dyes co-precipitated with the abietates ('rosinates'), are subject to spontaneous ignition, either in the freshly ground state, or as bulk material in drying ovens while a little moisture remains.

See METAL ABIETATES

ROTANES **$(C_7H_4)_n$**

1. de Meijere, A. *et al., Angewand. Chem. (Int.)*, 1995, *34*(7), 781; *Chem. Eur. J.* 1995, **1**(2), 124
2. Bunz, U. H. F. *et al., J. Amer. Chem Soc.*, 2002, **124**, 13814

The cyclic oligomers of 3-(1,2-Ethylidene)penta-1,4-diyne-1,5-diyl, (n = 5,6,7,8), obtained by oxidative coupling of 1,1-Diethynylcyclopropane, are called 'exploding rotanes'. They live up to the name, being sensitive to heat, friction or shock and having some 6 kJ/g available energy (TNT; 4.3 kJ/g). Higher homologues (n = 9,10,12) are probably no more stable, but are not yet reported as exploding; lower would be still less stable but are not known. The pentamer demolished a melting-point apparatus when a melting point was attempted. The permethylated rotanes do not explode similarly, although at most a third of the energy of the spiropropanes would be attributable to the cyclopropane ring [1]. Some ring fused (2 benzenoid, I metallocene) cycloundeca-

1,7,13-triene-3,5,9,11,15,17-hexaynes were found to explode on heating, to form carbon nanostructures, others did not. Explosion is claimed of nanosynthetic utitlity [2]. There is no reason to suppose that rotanes which are not polyacetylenic are unstable.

Pentaspiro[2.4.2.4.2.4.2.4.2.4]pentatriaconta-4,6,11,13,18,20,25,27,32,34-decayne, 3881

See also ANNULENES, NANOTECHNOLOGY

See other ALKYNES

RUBBER

Air, Cotton

Jones, S., *Res. Rept. 137*, Buxton, Safety in Mines Res. Est., 1956

If compressed air leaks from a rubberised cotton hose and causes squealing vibration to occur, enough heat may be generated to cause ignition. Fires have been started by squealing of poorly patched hoses, and ignition sources have been caused by use of rubberised cotton gaskets (cut from used conveyor belting, etc.) in plain flanged joints.

Metal azides

Tanaka, J. *et al., Chem. Abs.*, 1952, **46**, 11743h

During the preparation of cellular rubber by thermal decomposition of calcium, strontium or barium azides, various additives were necessary to prevent explosive decomposition of the azide in the blended mixture.

Sodium chlorate

See Sodium chlorate: Aluminium, Rubber

RUNAWAY REACTIONS

1. *Runaway Reactions, Unstable Products and Combustible Powders*, Symp. Ser. No 68, Rugby, IChE, 1981
2. Various authors, *J. Loss Prev.*, 1993 **6**(2)
3. *Safety and Runaway Reactions*, Smeder, B & Mitchison, N. (Eds.), EUR 17723 EN, European Commission, 1997
4. Chen, J. R. *et al., Process Safety Progr.*, 1998, **17**(4), 259
5. *Int. Symp. Runaway React., Pressure Relief Design, and Effluent Handling*, Melhem G. A. & Fisher, H. G. (Eds), New York, American Inst. Chem. Engineers
6. Bosch, J. *et al., Ind. & Eng. Chem. Res.*, 2004, **43**(22), 7019
7. Balasubramanian, S. G. et al., *Proceedings of 36th Annual Loss Prevention Symposium*, 2002, 511, Amer. Inst. Chem. Eng.

The 22 papers of the symposium [1] were presented under the headings: Theory, Laboratory Studies, Calorimetry (2 sessions), Applications. Several papers are devoted to individual instrumental methods of measuring and assessing potential for exothermic runaway reactions to develop. An issue of the *journal of Loss Prevention in the Process Industries* is devoted to a variety of, mostly calorimetric, studies of runaway reactions [2]. The proceedings of a European Union Seminar in 1994 appear as a book, including hard data as well as debate about such matters as operator training [3]. Summary of runaway reaction and loss of containment incidents in Taiwan 1978-96, showed polymerisation to be most dangerous assigned operation. Peroxides led monomers by 13 to 5 as hazards. Peroxide explosions are listed in more detail [4]. A symposium proceedings includes many papers on runaway reactions [5]. The topic continues to be much discussed [7], mostly with a view to defining the potential for runaway, to a lesser degree stopping a runaway once started (especially applicable to radical polymerisations). For the latter purpose, you must first detect runaway in real time [6]. In the editor's experience engineers often neglect to consider that thermocouple pockets may engender a lag of some minutes in temperature monitoring, while substantial pressure deviations may only appear very late in a runaway process.

Examples of runaway reactions may be found in the entries:
Aluminium chloride, : Alkenes, 0062
Butyrolactone, : Butanol, 2,4-Dichlorophenol, Sodium hydroxide, 1524
Chlorine, 4041
2,4,-Dichloronitrobenzene, : Acetic acid, Potassium fluoride, Dimethylacetamide, 2097
Dichloronitrobenzene, : Aniline, 2096
† Ethylene oxide, : Ammonia, 0825
† Ethylene oxide, : Glycerol, 0825
† Formaldehyde, : Phenol, 0415
Nitric acid, : 1-Nitronaphthalene, Sulfuric acid, 4430
Nitric acid, : Formic acid, Urea, 4430
Nitric acid, : Nitrobenzene, Sulfuric acid, 4430
Sodium molybdate, 4708
1,2,4,5-Tetrachlorobenzene, : Sodium hydroxide, Solvent, 2072
2,4,6-Trichloro-1,3,5-triazine, 1035
See also CALORIMETRY, POLYMERISATION INCIDENTS

RUST

Rust (a complex hydrated basic iron carbonate) is one of the most common contaminants in non-stainless steel plant, and has been involved, usually catalytically, in many different types of hazardous incident.
Carbon disulfide: Air, Rust
Hydrazine: Rust
Hydrogen sulfide: Rust
Magnesium: Metal oxides (reference 3)
THERMITE REACTIONS
See FRICTIONAL IGNITION OF GASES AND VAPOURS

SAFE STORAGE OF CHEMICALS

Pipitone, D., (Ed.), *Safe Storage of Laboratory Chemicals*, New York, Wiley, 1984
This book in 2 parts and 9 chapters with 6 appendices covers all aspects of the requirements for safe storage of chemicals for laboratories. The first part consists of 5 chapters:

Steere, N. V. Storage requirements for flammable and hazardous chemicals.

Bretherick, L. Incompatible chemicals in the storeroom: identification and segregation.

Nicholls, L. J. Labeling unstable chemicals.

Pipitone, D. A. Counteracting chemical spills in the storeroom.

Macenski, A. G. Use and selection of computers for chemical tracking systems.

The second part of the book contains 4 chapters on case histories and studies relating to chemical storage, and the appendices deal with specific aspects of labeling, purchasing chemicals, microcomputing, safety equipment, flash points of solvents and a safety checklist. A revised second edition is in press.

SAFETY LITERATURE

1. Editor's opinion, 2004
2. Agam, G. *Org Process R. & D.*, 2004, **8**(6), 1042

Many of the proliferating compendia of chemical safety information are composed in an unthinking, formulaic and plagiaristic manner, by persons or machines knowing no chemistry, giving rise to ramifying errors. These are usually on the side of safety (but not always so). An example in both the major multi-volume English language works was, until lately, the section: 'heating to decomposition'. Thus both reported sodium azide as giving nitrogen oxides, in which case car air-bags, which work by heating sodium azide to decomposition, must be extremely dangerous, both by virtue of the highly poisonous fumes discharged into the passenger compartment and by probable radiation from the nuclear transmutation evidently involved. There is a persistent inability to distinguish between pyrolysis and combustion combined with an automatic assumption that both give rise to the oxides of the elements present (except those of halogens) and to nothing else. Many nitrogenous compounds give much more hydrogen cyanide, even in circumstances of combustion, but this is rarely, if ever, mentioned (nor, apparently, are elemental halogens ever evolved when chlorine and bromine containing materials are burnt). Nitrogen oxides most commonly arise from heating empty air, and air is also omitted from consideration in those entries which report common (combustible) solvents exploding on heating. Some of these errors have been copied into safety data sheets issued by supposedly authoritative chemical societies. Even as one source of error is moderated, another may hasten to replace it [1].

The datasheets which now accompany pure or bulk chemicals, even from laboarory supply houses, are becoming rapidly more credible, thus trustworthy [1]. However two surveys of Material Safety Datasheets (MSDSs), apparently largely for compounded formulations, showed that only a tenth were judged both adequate and correct, while two thirds were both inadequate and in error [2]. *Errare est humanum* – this handbook, too, may contain errors while certainly holding reports, accident explanations and claims of hazard which the editor does not believe (usually indicated in phraseology or cross-reference). Nor is it automatically to be assumed that all listed and cross-indexed components of complex mixtures contributed to the accidents reported. Accept nothing uncritically!

SAMARIUM(II) COMPLEXES ON SILICA

Nagl, I. *et al., J. Amer. Chem. Soc.*, 2000, **122**(7), 1544

Mesoporous silica supported complexes of samarium(II), also having an amine and tetrahydrofuran ligand, were found to incandesce on exposure to air. The initial deposition was from samarium(II) bis(dimethylsilyl)amide, and bis(dimethylsilyl)amine is itself not a compound likely to be air stable.

SAMPLE DISSOLUTION

1. Bock, R., *Handbook of Decomposition Methods in Analytical Chemistry*, (Marr, L., translator and reviser), Glasgow, International Textbook Co., 1979
2. IUPAC Anal. Chem. Div., *Pure Appl. Chem.*, 1984, **56**, 479—489
3. Kingston, H. M. *et al., Anal. Chem.*, 1986, **58**, 2534—2541
4. Tattersall, P. J., *Lab. Practice*, 1986, **35**(10), 95
5. Bedson, A., *Chem. Brit.*, 1986, **22**, 894
6. Nakashima, S. *et al., Analyst* (London), 1988, **113**, 159—163

Of the 444 pages, 165 deal with oxidising procedures for analytical samples, and the hazards involved are detailed with suitable precautions [1]. The use of acid pressure decomposition methods in trace element analysis is reviewed (61 references). Vessels of high purity materials (PTFE, glassy carbon) within compact metal pressure casings are used. At 170°C, the temperature and considerable autogenous pressure enhance greatly the reaction capacity of acids and oxidising agents, permitting rapid dissolution of a wide range of samples. Critical aspects of vessel design and operational use are detailed [2]. The use of microwave heating to heat closed Teflon PFA vessels containg organic samples and various mineral acids has been investigated, with measurement of temperature profiles in the digestion vessels [3]. The technique has also been applied to other agricultural samples [4]. Use of microwave oven heating to accelerate sample dissolution has been reviewed [5]. Comparative tests on sealed and pressure-relieved digestion vessels with microwave heating have been reported, with nitric—perchloric acid mixtures to digest marine biological samples, and with hydrofluoric—nitric—perchloric acid mixtures to digest marine sediments [6].

Some examples of incidents are detailed under:

Hydrogen peroxide, : Organic materials, Sulfuric acid, 4471
Nitric acid, : Organic matter, Sulfuric acid, 4430
Perchloric acid, : Nitric acid, Organic materials, 3992
Potassium chlorate, : Nitric acid, Organic materials, 4011
MICROWAVE OVEN HEATING

SCALE OF WORK

1. Editor’s comments
2. Gygax, R. W., *Chem. Eng. Progress*, 1990, (Feb.), 53
3. *Chemical Reaction Hazards,*, Barton, J. & Rogers, R., Rugby, IChE, 1993
4. Anon., *Loss Prev. Bull.*, 1992, (105) 15
5. *Org. Proc. Res. Dev.*, Amer. Chem. Soc.

Nothing is so explosive that 1 mg is a significant danger. But with 1 tonne of sodium bicarbonate (baking soda), injudiciously mixed with weak acid (vinegar), it is quite possible to blow a reactor apart, with consequent fatalities. This consideration should be held in mind when using this text. Educators might also consider that, though they will have no accidents if they arrange practical work exclusively on the micro-scale, they will create very dangerous graduates who have no idea how to handle danger, nor even where it may lie, should they enter the world of real chemistry.

The problems of scale-up generally arise from the transfer of heat through the walls of a vessel, or the egress of gases and vapours through a hole in the wall. Rates of both of these, being surface phenomena, increase as the square of the linear dimensions of similar vessels. However, the contents, and associated potential energies, increase as the cube. It is also the case that the pressure a vessel can contain decreases sharply with size if similar materials of construction are used [1].

For a study of methods of assessment of thermal runaway risk from laboratory to industrial scales [2]. A more detailed but eminently clear treatment of this and other needful safety considerations on scaling reactions up to production has since been published [3]. So slight a scale-up as replacing two charcoal filters by one bigger one may cause a fire because heat loss was reduced [4]. A journal devoted to scale-up of organic chemical processes has been available from 1996 [5], while *J. Hazardous Materials* is (2004) devoting increasing space to rendering averagely risky syntheses and materials operable on industrial scale.

Heat, and sometimes gas, transfer from the core of a bulk material, also influences auto-ignition and explosion. The concept of critical mass is not limited to nuclear explosives (though shape is also important). Some entries in this text, such as sodium chlorate, ammonium nitrate and ammonium perchlorate, have proved extremely destructive during industrial storage by the tens of tonnes, but are incapable of explosion at the ten gramme scale. Many other entries are for hazards significant only beyond laboratory scale [1].

See tert-Butyl hydroperoxide, transition metal salts
See also ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

SELF-ACCELERATING DECOMPOSITION TEMPERATURE (SADT)

Fisher, H. G. *et al., J. Loss Prev.*, 1993, **6**(3), 183

SADTs, a measure of safe storage and drying temperatures for industrial products, are determined by a variety of techniques, often large scale with up to 200 kg samples. Smaller scale calorimetric methods are discussed.

See also CALORIMETRY, SELF-HEATING AND IGNITION INCIDENTS

SELF-ACCELERATING REACTIONS

Brogli, F. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 665—683, Basle, SSCI, 1980

The general characteristics, contributory factors and potential hazards arising from self-accelerating (sometimes autocatalytic) reactions are discussed, together with the means to identify such reaction systems and appropriate practical precautions. Five product classes showing dangerous self-acceleration tendencies are aromatic nitro compounds, aliphatic *N*-nitroso compounds, thiophosphate esters, acrylates (and acrylonitrile and acrylamide), and sulfones or esters and chlorides of sulfonic acids. Four types of reaction similarly assessed are organic reactions with metals (Béchamp, Grignard), Bucherer amination, Friedel-Crafts with nitro compounds, and condensations with cyanuric chloride. 11 Examples of hazardous chemicals or reaction mixtures discussed in detail are the entries:

Aluminium chloride, : Nitrobenzene, 0062
Ammonium hydrogen sulfite, 4540
Benzyltriethylammonium permanganate, 3611

Bis(4-hydroxyphenyl) sulfone, 3491
2-Chloro-5-nitrobenzenesulfonic acid, 2137
1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione, 1859
† Dimethyl sulfoxide, 0917
† Methyl acrylate, 1526
N-Methyl-*N*-nitrosourea, 0871
Nitric acid, : 2-Aminothiazole, Sulfuric acid, 4430
3-Nitrobenzenesulfonic acid, 2261
Sodium hydride, : Dimethylformamide, 4438
Succinodinitrile, 1429
Sulfuric acid, : 4-Chloronitrobenzene, Sulfur trioxide, 4473
2,4,6-Trichloro-1,3,5-triazine, 1035
2,4,6-Trichloro-1,3,5-triazine, : Acetone, Water, 1035

SELF-HEATING AND IGNITION INCIDENTS

1. Virtala, V. *et al., Chem. Abs.*, 1952, **44**, 7770i—7771b
2. Napier, D. H. *et al., Runaway Reactions*, 1981, Paper 2/F, 1—15
3. Bishop, R. C., *Runaway Reactions*, 1981, Paper 2/H, 1—4
4. Duane, T. C. *et al., Runaway Reactions*, 1981, Paper 2/J, 1—8
5. Kotoyori, T. *et al., Thermochim. Acta*, 1983, **67**, 35—44
6. Bowes, P. C., *Self-Heating: Evaluation and Control*, London, HMSO, 1984
7. Chervin, S *et al., J. Haz. Mat.*, 2004, **115**(1-3), 107

Methods for assessing the potential for oxidative self-heating and ignition of a range of 25 organic liquids and solids were described. Case histories are included for ignition of castor oil on peat, mineral oil on iron turnings, and wood shavings as lagging round steam pipes at 100°C, with 56 references [1]. Oxidative self-heating behaviour in mixtures of beech sawdust and raw linseed oil, in presence or absence of water (which accelerates heating) was studied to gain insight into the basic processes involved in ignition of such 2-phase systems [2]. Self-ignition phenomena in powdered grain products, corrugated fibreboards, iron powder, contaminated mineral lagging, and tobacco [3], and also spray drying of milk powder [4] were studied. An adiabatic self-heating process recorder allows very strictly adiabatic self-heating tests to be carried out accurately and easily on small samples of a wide range of chemical materials [5]. A book reviews the theoretical background and practical applications of methods of assessing the phenomena [6]. A method for classifying self-heating materials for transport purposes, using small-scale experimental tests in combination with activation energy, is described [7].

Some self-heating and ignition incidents will be found in the entries:

Adipic acid, 2435
1,4-Benzoquinone, 2207
† 1,3-Butadiene, 1476
Cinnamaldehyde, 3128
Copper iron(II) sulfide, 4263
Dibromomethylborane, 0425
† Di-*tert*-butyl peroxide, 3069

Dichlorine oxide, : Hydrocarbons, 4089
* Dimethyl terephthalate, 3286
† Hydrogen sulfide, : Soda-lime, 4477
Iron disulfide, 4395
Iron, : Air, Oil, 4382
* Methoxy-1,3,5,7-cyclooctatetraene, 3143
Nitric acid, : Ion exchange resins, 4430
1-Nitroso-2-naphthol, 3244
Sodium dichromate, : Sulfuric acid, Trinitrotoluene, 4244
Sodium nitrite, : Paper, Sulfur, 4715
ALDEHYDES
CELLULOSE NITRATE: Iron red, etc.
MILK POWDER
POLYPROPYLENE POWDER
SOAP POWDER
See also IGNITION SOURCES, INSULATION

SEMICONDUCTOR FABRICATION

1. Chen, J. R., *Process Safety Progress*, 2002, **21**(1), 19
2. *Handbook of Speciality Gas Safety in Semiconductor Industry*, Kondo, S. (Ed.), Jap. Soc. for Safety Eng., 1996

Although the small scale of operations limits risk to life, but not to property, integrated circuit manufacture offers special problems of fire prevention, chiefly by reason of use of highly reactive, often pyrophoric, gases such as silanes and germane. Some incidents are reported. Some flammability values are given for silane, dichlorosilane, hydrogen, phosphine and ammonia in gaseous oxidants such as chlorine trifluoride, fluorine, nitrogen trifluoride and nitrous oxide [1]. The references include some central to the topic, including [2].

SILANES $H(SiH_2)_nH$, $RSiH_3$, etc.

1. Stock, A. *et al., Ber.*, 1922, **55**, 3961
2. Kirk-Othmer, 1983, Vol. 20, 888
3. Ullmann, 1993, **A24**, 31 & 35

All the lower silanes are extremely sensitive to oxygen and ignite in air. The liberated hydrogen often ignites explosively [1]. Only under certain critical experimental conditions can they be mixed with oxygen without igniting [2]. Alkyloxysilanes can disproportionate to give silanes under base catalysis. Poly(alkyl)oxasilanes may depolymerise and disproportionate to give alkylsilanes and poly(alkyl)oxosiloxanes [3].

Individually indexed compounds are:
* Azidosilane, 4496
† Disilane, 4564
* Disilyl oxide, 4560
* Disilyl sulfide, 4563
* Oxodisilane, 4525
* Oxosilane, 4470

* Poly(silylene), 4481
† Silane, 4534
† Tetramethoxysilane, 1758
Tetramethyldisiloxane, 1777
Tetrasilane, 4579
* Tetrasilylhydrazine, 4580
† Trisilane, 4574
* 2,4,6-Trisilatrioxane, 4561
* Trisilylamine, 4575
* Trisilylarsine, 0102
* Trisilylphosphine, 4578

See Oxygen: Tetramethyldisiloxane

See other NON-METAL HYDRIDES

Chloroform, or Carbon tetrachloride, Oxygen

Stock, A. *et al., Ber.*, 1923, **56**, 1087

The chlorination of the lower silanes by halogenated solvents proceeds explosively in presence of oxygen, but catalytic presence of aluminium chloride controls the reaction.

Halogens

Stock, A. *et al., Ber.*, 1919, **52**, 695

Reaction of silanes with chlorine or bromine is violent.

Olefins, Platinum

Mathias, L. J. *et al., Chem. Abs.*, 1995, **124**, 286890v

Si-H bonds add across olefins over platinum catalysts. This reaction (hydrosilation) is used in silicone polymer manufacture, when the silane is a hydrogen bearing oligo(alkylsiloxane). With some types of olefin there have been reports of runaways to explosion because of unexpectedly fast reaction. Dangerous substrates recorded are 2-allylphenols and ethenylsiloxanes. Very low levels of catalyst (ppm) and good cooling are recommended.

See also VINYLSILOXANES

SILICON COMPOUNDS

Groups or substances falling within this class are:

ALKYLHALOSILANES
ALKYLSILANES
HALOSILANES
ORGANOSILYL PERCHLORATES
SILANES
SILICONE GREASE
SILICONE LIQUID
SILICONE OIL
SILYLHYDRAZINES
TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES

SILICONE GREASE

Bromine trifluoride

See Bromine trifluoride: Silicone grease

SILICONE LIQUID **Poly(dimethylsiloxane)**

Silica powder, Unstated salt

Anon., *Loss Prev. Bull.*, 1987, (078), 9

A cosmetic preparation involved the vigorous dispersion of finely divided silica, and that of an ionically dissociable powder in a volatile silicone fluid. Small scale laboratory tests were uneventful, but in a preliminary 150 l manufacturing run, crackling noises were heard during the dispersion of silica powder, and on heating, the evolved vapour ignited. It was found that surface potentials of 35 kV could be measured 150 mm above the liquid. The static generation problem was completely eliminated by first dispersing the powdered salt component in the silicone liquid which effectively reduced the insulating properties of the silicone liquid.

See ELECTROSTATIC HAZARDS

SILICONE OIL

Yasufuku, S., *Chem. Abs.*, 1982, **96**, 220130

A major factor in ignition of dimethylsilicone oils after heating is the presence of a cyclic trimer. Flash point can be improved by addition of cerium acetylacetonate.

Contaminants

D'Onofrio, E. J., *Chem. Eng. News*, 1978, **56**(45), 51

Contamination of silicone oil baths with alkaline or acidic materials may lead to depolymerisation and a marked lowering of the flash point. This happened when the alkaline contents of a beaker heated in a silicone bath at 260°C frothed over into the oil, which itself then frothed and overflowed, exposing the electric immersion heater element which ignited the decomposition products.

Nitric acid

See Nitric acid: Silicone oil

SILVER COMPOUNDS

Many silver compounds are explosively unstable and/or powerful oxidants.

Individually indexed compounds are:

Bis(2-aminoethyl)aminesilver nitrate, 1767
* Cyclopentadiene—silver perchlorate, 1853
Diamminesilver permanganate, 0018
Dihydrazinesilver nitrate, 0019
Dipyridinesilver(I) perchlorate, 3261
Disilver cyanamide, 0304
Disilver diazomethanide, 0305
Disilver ketenide, 0567
Disilver ketenide—silver nitrate, 0568

Disilver pentatin undecaoxide, 0036
* Heptasilver nitrate octaoxide, 0047
Nitrogen triiodide—silver amide, 4629
1,3-Pentadiyn-1-ylsilver, 1809
Pentasilver diamidophosphate, 0046
Pentasilver orthodiamidophosphate, 0044
Phenylsilver, 2210
Silver 1,3,5-hexatrienide, 2046
Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide, 3599
Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide, 0039
Silver 2-azido-4,6-dinitrophenoxide, 2068
Silver 3,5-dinitroanthranilate, 2638
Silver 3-cyano-1-phenyltriazen-3-ide, 2666
Silver 3-hydroxypropynide, 1085
* Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1405
* Silver 4-nitrophenoxide, 2119
Silver 5-aminotetrazolide, 0391
Silver acetylide, 0565
* Silver acetylide—silver nitrate, 0566
Silver amide, 0015
Silver azide, 0023
Silver azide chloride, 0009
* Silver azidodithioformate, 0302
Silver benzo-1,2,3-triazole-1-oxide, 2120
Silver bromate, 0007
Silver buten-3-ynide, 1404
Silver chlorate, 0011
Silver chloride, 0008
Silver chlorite, 0010
* Silver chloroacetylide, 0563
* Silver cyanate, 0299
Silver cyanide, 0298
Silver cyanodinitromethanide, 0564
Silver cyclopropylacetylide, 1832
Silver difluoride, 0014
Silver dinitroacetamide, 0685
Silver fluoride, 0013
Silver fulminate, 0300
Silver hexahydrohexaborate(2—), 0027
Silver hexanitrodiphenylamide, 3423
Silver hyponitrite, 0031
Silver imide, 0030
Silver iodate, 0020
* Silver isophthalate, 2882
Silver malonate, 1068
Silver nitrate, 0022

Silver nitride, 0038
Silver *N*-nitrosulfuric diamidate, 0016
Silver *N*-perchlorylbenzylamide, 2730
Silver osmate, 0034
Silver oxalate, 0569
Silver perchlorylamide, 0028
Silver permanganate, 0021
Silver peroxochromate, 0037
Silver phenoxide, 2211
Silver phenylselenonate, 2212
Silver phosphinate, 0017
Silver sulfide, 0035
Silver tetrafluoroborate, 0005
Silver tetrafluorobromate, 0006
Silver tetrazolide, 0365
Silver trichloromethanephosphonate, 0303
Silver trifluoropropynide, 1026
Silver trinitromethanide, 0301
Silver trisulfurpentanitridate, 0024
Silver—aluminium alloy, 0002
Silver(I) oxide, 0032
Silver(II) oxide, 0025
Tetrasilver diimidodioxosulfate, 0043
Tetrasilver diimidotriphosphate, 0042
Tetrasilver orthodiamidophosphate, 0041
* Tetrasulfurtetraimide—silver perchlorate, 0029
1,2,4-Triazolo[4,3-*a*]pyridine—silver nitrate, 2263
Trisilver tetranitride, 0040

See METAL ACETYLIDES
See other HEAVY METAL DERIVATIVES

SILVER-CONTAINING EXPLOSIVES

1. Luchs, J. A., *Photog. Sci. Eng.*, 1966, **10**, 334
2. MacWilliam, E. A. *et al., Photog. Sci. Eng.*, 1977, **21**, 221—224

Silver solutions used in photography can become explosive under a variety of conditions. Ammoniacal silver nitrate solutions, on storage, heating or evaporation eventually deposit silver nitride (‘fulminating silver’). Silver nitrate and ethanol may give silver fulminate, and in contact with azides or hydrazine, silver azide. These are all dangerously sensitive explosives and detonators [1]. Addition of ammonia solution to silver containing solutions does not directly produce explosive precipitates, but these are formed at pH values above 12.9, produced by addition of alkali, or by dissolution of silver oxide in ammonia [2].

See Silver nitrate: Ammonia, etc.
See also FULMINATING METALS, SILVERING SOLUTIONS, TOLLENS’ REAGENT

SILVER-CONTAINING RESIDUES

1. Wakeford, D. H., *School Sci. Rev.*, 1978, **59**(209), 665—666
2. Perman, C. A., *Talanta*, 1979, **26**(7), 603—604

A simple and economical method for recovering silver residues by dissolution in used photographic fixer (thiosulfate) solution, then precipitation by addition of zinc powder, is detailed [1]. After the acid digestion phase of silver recovery operations, addition of ammonia followed immediately by addition of ascorbic acid as reducant gives a near-quantitative recovery of silver metal, and avoids the possibility of formation of silver nitride [2].

SILVERING SOLUTIONS

1. Smith, I. C. P., *Chem. & Ind.*, 1965, 1070; *J. Brit. Soc. Glassblowers*, 1964, 45
2. Ermes, M., *Diamant*, 1929, **51**, 62, 587
3. Loman, E., and Mylius, W., *Diamant*, 1929, **51**, 526, 42
4. Sivertz, C. *et al.*, Ger. Pat. 2 162 263, 1972

Brashear's silvering solution (alkaline ammoniacal silver oxide containing glucose) or residues therefrom should not be kept for more than 2 hours after preparation, since an explosive precipitate forms on standing [1]. The danger of explosion may be avoided by working with dilute silver solutions (0.35M) in the Brashear process, when formation of $Ag(NH_3)_2OH$ (and explosive $AgNH_2$ and Ag_3N therefrom) is minimised. The use of Rochelle salt, rather than caustic alkali, and shielding of solutions from direct sunlight, are also recommended safeguards [2,3]. Addition of sodium gluconate or tartrate to ammoniacal silver salt—base mixtures inhibits the formation of fulminating silver [4].

See FULMINATING METALS, TOLLENS' REAGENT

SILVER—NITROGEN COMPOUND HAZARDS

Anon, *CISHC Chem. Safety Summ.*, 1978, **49**, 29

A silver-containing solution was basified with sodium hydroxide, and after filtration, ammonia solution was used to wash residual silver from the filter. Hydrazine sulfate was then added to precipitate metallic silver and when the mixture was heated it exploded. This may have been caused by formation of silver nitride and/or hydrazine—silver complexes, both of which are explosively unstable.

Silver chloride: Ammonia

Silver nitrate: Ammonia, Sodium hydroxide

See FULMINATING METALS, SILVER-CONTAINING EXPLOSIVES, TOLLENS' REAGENT

SILYLHYDRAZINES $(R_3Si)_2NNHSiR_3$, etc.

Oxidants

1. Wannagat, U. *et al., Z. Anorg. Chem.*, 1959, **299**, 341—349
2. Wannagat, U. *et al., Monats.*, 1966, **97**, 1157—1162

During analysis of a series of tris(organosilyl)hydrazines, treatment with 1 : 1 mixtures of nitric and sulfuric acids had caused explosive reactions [1]. Subsequently the hypergolic behaviour of a range of 20 silylhydrazines and congeners in contact with fuming nitric acid was examined. All di- or tri-silyl derivatives showed ignition delays of 10 ms or less, several also exploding after ignition. All the derivatives ignited on dropping into gaseous fluorine, and into conc. liquid ozone—oxygen mixtures, most also exploding in the latter [2].

The most reactive compounds are:
1,2-Bis(triethylsilyl)hydrazine, 3577
1,2-Bis(triethylsilyl)trimethylsilylhydrazine, 3689
1,2-Bis(trimethylsilyl)hydrazine, 2612
1,2-Bis(tripropylsilyl)hydrazine, 3771
Dilithium 1,1-bis(trimethylsilyl)hydrazide, 2591
1,2-Dimethyl-2-trimethylsilylhydrazine, 2041
Lithium 2,2-dimethyltrimethylsilylhydrazide, 2035
3,3,6,6-Tetraphenylhexahydro-3,6-disilatetrazine, 3846
Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine, 3580
Tris(trimethylsilyl)hydrazine, 3224
See other N-METAL DERIVATIVES

SINTERED GLASS

The recent replacement, in many laboratories, of filter papers and Buchner funnels by sintered, or fritted, glass filters when isolating solids has increased explosion hazards in two ways. Firstly, fritted glass is an excellent surface on which to induce detonation by scraping a solid. Secondly, the sinters rapidly clog and are valuable enough to encourage cleaning with powerful oxidant reagents rather than disposal, sometimes resulting in explosions from reaction with solvent or other materials impregnating the frit. The editor also finds it difficult to clean the porous support such that contamination of subsequently filtered solid is avoided and impossible to recover as much product as from a filter paper.

See Nitric acid: Glassware, Hydrogen peroxide, 5-Bromo-4-pyrimidinone
See also CLEANING BATHS FOR GLASSWARE, FRICTIONAL INITIATION INCIDENTS

SLAG WOOL

Potassium permanganate
See Potassium permanganate: Slag wool

SMELT

1. Nelson, W., *Chem. Abs.*, 1973, **78**, 126458
2. Morgan, H. W. *et al., Chem. Abs.*, 1967, **66**, 56874t
3. Anon., *Chem. Abs.*, 1967, **66**, 56876v
4. Duda, Z., *Chem. Abs.*, 1976, **84**, 32851
5. Kashtanov, V. S., *Chem. Abs.*, 1979, **91**, 41112
6. Shivgulam, M. *et al., Pulp Pap. Can.*, 1979, **80**(9), 89—92
7. Gardner, H. S., US Pat. 4 194 124, 1980
8. Kohl, A. L. *et al., Tappi J.*, 1986, **63**(9), 82—85
9. Gairns, S. A. *et al., Pulp Pap. Can.*, 1996, **97**(6), 46

'Smelt', the residue from 'burning' (high temperature combustive evaporation, sometimes with submerged burners) of spent sulfite liquor from wood-pulp treatment and consisting largely of sodium sulfide and sodium carbonate, explodes violently on contact with water while still hot. The mechanism is discussed [1], and operational procedures to avoid the possibility of explosions are recommended [2,3]. A further possible cause of explosions is the generation of hydrogen and/or hydrogen sulfide at the high temperatures involved [4]. Equipment used for processing kraft liquor is classified on the basis of explosion and fire hazards [5]. Addition of sodium or potassium chloride to smelt reduces the eutectic m.p. and the tendency to spout plugging and dissolving tank explosions, but increases the corrosion rate [6]. Smelt—water explosions are suppressed by the radiochemical nucleation of bubbles. No explosions occurred when cold water was dropped into molten sodium chloride at 1000°C under γ-irradiation at 4300 rad/min [7]. The probability and intensity of explosions in smelt—water systems is reduced by increase in pressure and temperature [8]. Experiment shows that pyrolysis of liquors at high temperatures in non-oxidising atmosphere can generate char particles containing substantial levels of metallic sodium, from reduction of sodium carbonate by carbon. This char may be pyrophoric and will certainly evolve hydrogen on contact with water; this is suggested as the principal cause of explosions [9].

See SUPERHEATED LIQUIDS

SOAP POWDER

Anon., *Chem. Abs.*, 1935, **29**, 6759.7

General factors affecting spontaneous ignition of soap powders were discussed.

SODA—LIME $NaOH.Ca(OH)_2$

Hydrogen sulfide

Bretherick, L., *Chem. & Ind.*, 1971, 1042

Soda—lime, after absorbing hydrogen sulfide, exhibits a considerable exotherm (100°C) when exposed simultaneously to moisture and air, particularly with carbon dioxide enrichment, and has caused fires in laboratory waste bins containing moist paper wipes. Saturation with water and separate disposal in sealed containers is recommended.

SODIUM CARBOXYMETHYLCELLULOSE

Hydrogen peroxide, Iron(II) sulfate, Nitric acid

See Hydrogen peroxide: Iron(II) sulfate, Nitric acid, etc.

'SODIUM PERCARBONATE' Various structures, below

Acetic anhydride

1. Anon., *Lab. Accid. in Higher Educ.*, item 20, HSE, Barking, 1987
2. Author's comment, 1989

Mixing 'sodium percarbonate' with acetic anhydride led to explosive shattering of the flask [1], undoubtedly caused by the formation of acetyl peroxide. The name 'sodium

percarbonate' has been used indiscriminately to describe 3 different compounds, all of which would react with acetic anhydride to give extremely explosive acetyl peroxide [2]. These are sodium monoperoxycarbonate, NaOCO.OONa, [4452-58-8]; sodium peroxydicarbonate, NaOCO.OOCO.ONa, [3313-92-6]; and sodium carbonate sesqui hydrogen peroxidate, NaOCO.ONa . $1.5H_2O_2$, [15630-89-4].
See other PEROXOACID SALTS

SODIUM PRESS

Blau, K., private comm., 1965
The jet of a sodium press became blocked during use, and the ram was tightened to free it. It suddenly cleared and a piece of sodium wire was extruded, piercing a finger, which had to be amputated because of severe necrosis. Sodium in a blocked die should be dissolved out in a dry alcohol.
See Potassium: Alcohols

SODIUM TETRAAZIDOMETALLATES

Sussek, H. *et al., Eur. J. Inorg. Chem.*, 2000, (3), 455
Sodium tetraazidoaluminate complexed by pyridine and tetrahydrofuran and analoguous indium and gallium derived materials were obtained, the last uncomplexed. They are explosive on rapid heating, sodium tetraazidogallate at 150 C, and shock sensitive.
See other METAL AZIDES

SOLVATED OXOSALT INCIDENTS

1. Bretherick, L., *Chem. Eng. News*, 1983, **61**(50), 2
2. Raymond, K. N., *Chem. Eng. News*, 1983, **61**(49), 4
3. Wolsey, W. C., *J. Chem. Educ.*, 1973, **50**(6), A335
4. Cotton, F. A. *et al., J. Amer. Chem. Soc.*, 1960, **82**, 2986
5. Sandstrom, M. *et al., Acta Chem. Scand.*, 1978, **A32**, 610
6. Cook R. E. *et al., J. Chem. Res.*, 1982, (S) 267, (M) 2772
7. Forsberg, J. H., *Chem. Eng. News*, 1984, **62**(6), 33
8. Bretherick, L., *Chem. Eng. News*, 1990, **68**(22), 4

Several instances of apparently stable solvated metal perchlorates being converted by partial desolvation into explosively unstable materials indicate that this may be a more common potential hazard than has been realised [1]. Neodymium perchlorate tetra-solvated with acetonitrile (obtained by vacuum evaporation of the solution at ambient temperature) had not been found to be thermally- or shock-sensitive, but when vacuum dried at 80°C to the di-solvate, it exploded violently on contact [2]. Erbium perchlorate tetrasolvated with acetonitrile had likewise appeared stable, but when vacuum dried at 150°C to a glassy solid which still contained some solvent, it too exploded when scraped with a spatula [3]. Mercury(II) perchlorate hexa-solvated with DMSO appears stable [4], but when dried to the tetrasolvate, it is impact- and friction-sensitive [5]. The fact that the solvating species may also be water suggests that this is not a direct effect of a perchlorate oxidising an organic solvent. Thus, cobalt(II) perchlorate hexahydrate is a common commercial (and stable) chemical, but when overheated during final drying which converted it to a trihydrate, the latter exploded under slight impact, and was later shown to be endothermic [6]. It is suggested that there is a need for closer control and documentation of drying procedures for solvated metal perchlorates [1]. An incident is reported where a solution of a lanthanide metal perchlorate in acetonitrile detonated during heating under reflux [7].

A possible explanation of the reduced stability of the lower organic solvates may be connected with the effect of reduced solvation upon the oxygen balance of the salts. Unsolvated metal perchlorates have an apparent balance of +700%, and solvation with 4 mols of acetonitrile reduces this to —46.3%, and with 4 or 6 mols of DMSO to —43% and —28.6% respectively. Desolvation to 2.18 mols of acetonitrile, or to 2.0 mols of DMSO, would give products of zero oxygen balance, with maximum energy release potential [8].

These and related incidents are detailed under:

† Acetonitrile, : Lanthanide perchlorate, 0755
Chromium(III) perchlorate . 6dimethyl sulfoxide, 4124
Cobalt(II) perchlorate hydrates, 4045
Erbium perchlorate, 4126
* Gallium perchlorate, 4129
Iron(III) perchlorate, 4056
Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide, 4073
Neodymium perchlorate . 2acetonitrile, 4142
Silver perchlorate, 0012

SOLVENT CABINETS

1. Anon., *Sichere Chemiearbeit*, 1997, **49**, 3
2. Editor’s Comments

After standing unopened for about a week, an unventilated solvent cabinet exploded violently, starting a fire which burnt out the laboratory. This was considered to have been a vapour/air explosion, not one caused by peroxide accumulation. The source of ignition was not clear, it might have been reactive drying agents. It is stated that the consequences would not have been as serious had the cabinet been ventilated [1]. To judge by the picture, the cabinet was of thin steel, offering negligible protection against heating by external fire. If it was like most of the solvent cabinets and bins known to the editor, the catch will probably also have been internal and made of sparking metal (although this explosion was not initiated by opening). A slight seepage of flammable solvent vapour seeping past a stopper in an open laboratory will be immediately dispersed by the ventilation. In the unventilated cabinets in which solvents have lately been kept, it is claimed as a safety measure, slight seepages of vapour will accumulate until they can form a substantial, enclosed, volume of explosive gases. A solvent cabinet designed for safety would be ventilated, thermally insulated, of non-sparking construction, and with blow-out panels. The majority of those the editor has met are none of these: they are potential explosive charges waiting to blow their door into the face of some unfortunate who sparks the explosion by turning the (sparking) catch [2].

See STORAGE OF CHEMICALS

SOLVENTS

1. Evon, S. E. *et al., Process Safety Prog.*, 1999, **18**(1), 1-4
2. Yarnell, A., *Chem. Eng. News*, 2002, **80**(20), 43
3. Various, *Chem. Eng. News*, 2002, **80**(25), 8, 10, 12
4. Editor's comments

It has been realised that reactions generally require the freedom of a liquid phase. Thus thermal stabilities of unstable materials are usually, but not always, less in solution than as the crystalline solid. Stability studies for processing should also evaluate solvent/reagent combinations. Appropriate solvent selection may much increase safety [1]. After fires during solvent redistillation in academia, it is suggested that purification be by chromatography through alumina, and that certainly distillation from active metals be avoided. Industrial sources query the academic habit of solvent redistillation, which often leaves the solvents more contaminated than they started and also removes stabilisers which inhibit formation of peroxides from, e.g. ethers, or phosgene from chlorinated solvents [2,3]. In the editor's experience, industrial solvents are usually extremely dry (and oxygen free) from the drum, by the time they have been transferred to bottles from a laboratory supplier less so, and after sitting around a laboratory for some months in part-used bottles may have acquired percentage levels of water, and equilibrium oxygen, from the air [4].

SPILLAGES

1. *How to Deal with Spillages of Hazardous Chemicals*, Poole, BDH Chemicals Ltd., 5th Edn., 1986
2. Melvold, R. W. *et al., J. Haz. Mat., 1988, 17, 329*—335
3. www.external.ameslab.gov/esha/lessons_learned/Yellow_Alerts/000427c 2000

A revised wall chart, with standardised disposal procedures for 396 toxic and hazardous chemicals, which is useful in the storeroom as well as in the laboratory [1]. A guidance manual has been developed by EPA in the US to assist in the selection and use of sorbent materials to control industrial spillages of hazardous liquids [2].

After a spillage of sulfuric acid, treated with a clay absorbent, the wastes were drummed up, along with some of the underlying soil. The sealed drum was later observed to be bulging. The lid blew off during venting, fortunately without causing injury. The underlying rock was limestone, which could itself have neutralised the spillage had it been left alone or simply hosed down [3]. Environmental concerns mean that spillages are treated with absorbents, then drummed up for later disposal. The absorbents are selected to be unreactive and usually warn of classes of chemicals with which they should not be used. They do not change the inherent properties of the spilt chemical, which may sometimes give rise to trouble when drummed up, especially since contaminants will also often be introduced. Drums for disposal should not be stored in occupied enclosed spaces and it is probably unwise that they be sealed while awaiting removal [Editor's comments].

See also Phenyloxirane

See DISPOSAL

See also ENVIRONMENTALISM, INSULATION

STARCH

NFPA 61A, Quincy (Ma), National Fire Protection Association, 1989

The new US fire code covers precautions to prevent fires or dust explosions in handling dried starch.

Energy of exothermic decomposition in range 260—340°C was measured as 0.461 kJ/g/

Cornstarch dust may be a dust explosion hazard.

See DUST EXPLOSION INCIDENTS (reference 33)

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Calcium hypochlorite, Sodium hydrogensulfate

See Calcium hypochlorite: Sodium hydrogensulfate, etc.

Nickel nitrate

See METAL NITRATES: Organic matter

STATIC INITIATION INCIDENTS

1. Krämer, H., *Chem. Ing. Tech.*, 1982, **55**, 419—428
2. Schaperklaus, H., Brit. Pat. 2004 476, 1979
3. Cartwright, P., *Chemtech*, 1991, **21**(11) 682
4. Britton, L. G., *Plant/Oper. Progr.*, 1992, **11**(2), 56
5. *Avoiding Static Ignition Incidents in Chemical Operations*, Britton L. G., AIChE, 1999
6. *Electrostatics – Code of Practice for the Avoidance of Hazards*, PD CLC/TR 50404, London, British Standards Inst., 2003

The current state of knowledge of charge generation in flowing or sprayed liquids was reviewed with 20 references, and criteria to allow assessment of ignition hazards were presented [1]. The risk of static sparks from thermoplastic bags or sacks was reduced by printing a grid of conductive ink on the surfaces [2]. A review of static electrical problems in the chemical industry, with further references, is found in [3]. Minimum Ignition Energies, with especial reference to electrostatic ignition, with tables of these and electrical properties of organic materials, are covered in [4]. Codes of practice for avoiding probl;ems have been published [5,6].

Ignition by static features in the entries:

∗ Bis(2-azidobenzoyl) peroxide, 3621
∗ Calcium hypochlorite, 3918
Calcium polysulfide, 3936
Chlorine dioxide, 4036
Chlorine, : Hydrogen(?), Sulfuric acid, 4041
† Chloroethylene, 0726
Ethyl acetate, 1613
Iron, : Polystyrene, 4382
Lead(IV) oxide, : Metals, 4828
Methylmercury perchlorate, 0432

Oxygen (Gas), : Biological material, Ether, 4825
Potassium chlorate, : Metal phosphinates, 4011
Potassium perchlorate, 4012
Sodium chlorate, : Paper, Static electricity, 4033
† Trichlorosilane, 4130
Tris(2,2′-bipyridine)chromium(II) perchlorate, 3868
See also ADHESIVE LABELS, IGNITION SOURCES, MINIMUM IGNITION ENERGY (MIE)

STATUARY

1. *Daily Telegraph*, (London), 2005, Oct. 1, p. 8
2. Editor's Comments

A workman went to seal a hole (presumably by hot work) in an aluminium tube statue, recently set on a concrete base. It exploded. This was attributed to combustible gases generated in the concrete [1]. It is conceivable that cement fired under reducing conditions contains some calcium carbide. However, it should be remembered that aluminium corrodes, or even dissolves, under alkaline conditions liberating hydrogen, possibly admixed with volatile hydrides of other elements present. Fresh cement is distinctly alkaline, and is only finally neutralised by atmospheric carbon dioxide over the course of months or years [2].

See Aluminium
See Calcium acetylide

STEAM EXPLOSIONS

1. Drumheller, D. S., *TOM MIX: A Computer Code for Calculating Steam Explosion Phenomena*, Rept. SAND-81-2520, Richmond (Va), USNTIS, 1982
2. Kolov, N. I. *et al., Kerntechnik*, 2000, **65**(5/6), 254; *ibid.*, 2001, **66**(1/2), 21

A mathematical model of the processes leading to steam explosions has been developed for the contact of hot liquids or molten solids dropping into water [1]. A review of detonation theory leads to an attempt to apply it to melt/water combinations, with particular reference to molten oxides in nuclear reactor melt-down. Alumina /water is more violent than urania/water [2].

See MOLTEN METAL EXPLOSIONS, SMELT, SUPERHEATED LIQUIDS, VAPOUR EXPLOSIONS

STEEL

1. Anon., *Fire Prot. Assoc. J.*, 1953, **21**, 53
2. Karim, G. A. *et al., J. Fire Sci.*, 1987, **5**, 272—285

Ignition can occur if steel wool (or a scouring pad) short-circuits the contacts of even a small dry-cell torch battery [1]. The ignition and combustion characteristics of steel wool, loosely packed in wire crates has been investigated in a heated air stream of 4 m/s. Autoignition temperatures above 377°C were recorded [2]. As a structural material, wet steel vessels can deplete the air within of oxygen by rusting, or by autoxidation of ferrous sulfide formed by contact with sulfur-containing materials. This has caused a number of deaths from asphyxiation and the sulfide has ignited

several fires. Hydrogen evolution is possible especially in contact with acids. Iron being a good catalyst for many reactions, trouble can also spring from this cause.
See Magnesium chloride: Air, etc., Sulfur dichloride: Iron

Apricots
Ontario Ministry of Labour, Internet information alert, 1997
A worker was killed while venting a bulging 45 gallon steel drum of apricot concentrate with a grinder. A grinder, the ultimate sparking tool, is not suitable for cutting into bulging food containers, which are more usually pressurised with hydrogen from interior corrosion than by the products of bacterial decay. However, bulging drums can kill without ignition.
See DRUMS

Silicon dioxide
See Silicon dioxide: Steel
See also RUST
See other IGNITION SOURCES

STORAGE OF CHEMICALS

1. *See entry* SAFE STORAGE OF CHEMICALS
2. Anon., *Loss Prev. Bull.*, 1988, (084), 19—22
3. Armstrong, B. S., *Loss Prev. Bull.*, 1988, (084), 23—31
4. Winder, C. *et al., J. Haz. Mat.*, 2000, **79**(1-2), 19

The book is an amplified version of papers presented at the 1982 ACS CHAS Div. Symposium on safe storage of laboratory chemicals. Chap. 2 deals with the segregation of incompatible reactive chemicals on a logical basis [1]. Two accounts of chemical warehouse fires emphasise the severe problems which arise from lack of proper segregation in storage of chemicals [2,3]. Academic study has reduced the problems of storage, both environmental and safety, to a system with an hundred subclassification groups. This solution seems likely to remain academic [4].
See also Ammonium peroxodisulfate: Sodium sulfide
See also EARTHQUAKE, SOLVENT CABINETS

STRAINED-RING COMPOUNDS

Three membered rings are all strained and the parent systems may be endothermic (ΔH_f°: cyclopropane 35; oxirane -78; aziridine 92; thiirane 52 kJ/mole). Some molecules with small distorted rings (of high strain energy) are explosively unstable. Individual entries are:

* 2-Azatricyclo[2.2.1.0^{2,6}]hept-7-yl perchlorate, 2361
† Azetidine, 1251
Benzvalene, 2282
Bicyclo[2.1.0]pent-2-ene, 1850
2-*tert*-Butyl-3-phenyloxaziridine, 3400
3-Chloro-1,3-diphenylcyclopropene, 3672
1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate, 3382
Cyanocyclopropane, 1459

† Cyclopropane, 1193
† Cyclopropyl methyl ether, 1603
2,3:5,6-Dibenzobicyclo[3.3.0]hexane, 3626
3,5-Dibromo-7-bromomethylene-7,7a-dihydro-1,1-dimethyl-1H-azirino[1,2-a]indole, 3467
2,2′-Di-*tert*-butyl-3,3′-bioxaziridine, 3353
Dicyclopropyldiazomethane, 2820
1,4-Dihydrodicyclopropa[*b,g*]naphthalene, 3446
N-Dimethylethyl-3,3-dinitroazetidine, 2844
Dinitrogen pentaoxide, : Strained ring heterocycles, 4743
† 1,2-Epoxybutane, 1604
† Ethyl cyclopropanecarboxylate, 2431
2,2′-(1,2-Ethylenebis)3-phenyloxaziridine, 3700
† Methyl cyclopropanecarboxylate, 1911
† Methylcyclopropane, 1576
1,2,3,-4,5, or -5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2062
† Oxetane, 1218
Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,2-dicarboxylic acid, 3255
Poly([7,8-bis(trifluoromethyl)tetracyclo [4.2.0.0^{2,8}.0^{5,7}]octane-3,4-diyl]-1,2-ethenediyl), 3457
Prismane, 2287
Spiro(homocubane-9,9$'$-diazirine) (Spiro[3*H*-diazirine-3,9^{-}pentacyclo[4,3,0,0^{2,5} 0^{3,8}0^{4,7}]nonane], 3121
Tetracyclo[4.3.0^{3,5}.0^{4,6}]nona-1,7-diene, 3119
3,6,9-Triazatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane, 2392
FURAZAN N-OXIDES
See also ENDOTHERMIC COMPOUNDS

STYRENE—BUTADIENE RUBBER

Emmons, H. W., *J. Appl. Polym. Sci.*, 1981, **26**, 2447—2457

Plioflex rubber heated to above 300°C may ignite spontaneously. The mechanisms of the thermal reactions involved are discussed.

See also RUBBER

SUGARS

Air, Base

1. Young, J. A., *Chem. Health & Safety*, 1998, **5**(1), 4
2. Nicloux, M., *Bull. Soc. Chim. Biol.*, 1928, **10**, 1135
3. Young, J. A., private communication, 1979
4. Bretherick, L, *Chem. & Ind.*, 1980, 164; *Chem. Brit.*, 1980, **16**, 184

A fatality from carbon monoxide poisoning is reported while cleaning out a milk tank with an alkaline cleanser [1]. Apparently autoxidation of reducing sugars, including lactose, can produce up to 3,000 ppm of carbon monoxide under moderately alkaline conditions [2]. This is only likely to be hazardous in confined spaces. Warnings of the possibility of poisoning in such circumstances from this curious, long known but little

remembered, reaction had been given earlier [3,4]. Although alkalis are much used in the sugar industry, sucrose is not a reducing sugar.
Lactose, 3551
See MILK POWDER

Sulfuric acid
See Sulfuric acid: Sucrose

Yeast
Dilute solutions of all sugars are subject to fermentation, either by yeast or by other micro-organism, or enzymes derived from these, producing gases which can pressurise and burst sealed containers. Some micro-organisms will produce hydrogen or methane, adding a fire and explosion hazard.
See CELLULOSE: WATER, YEAST

SULFINYL AZIDES $ArS(O)N_3$

Maricich, T. J. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 7771, 7776

Benzene-, *p*-nitrobenzene-, and *p*-toluene-sulfinyl azides are thermally unstable, decomposing explosively when warmed alone or as conc. solutions. They may be prepared safely and handled as solutions at —20°C or below. The isolated solids may be stored at —80°C, but benzenesulfinyl azide explodes at 11°C, and *p*-toluenesulfinyl azide at 8°C. Individually indexed compounds are:
Benzenesulfinyl azide, 2266
4-Nitrobenzenesulfinyl azide, 2197
4-Toluenesulfinyl azide, 2776
See other ACYL AZIDES

SULFONATION INCIDENTS

1. Anon., *Loss Prev. Bull.*, 1979, (030), 159
2. Brogli, F. *et al., Runaway Reactions*, 1981, Paper 3/M, 4—5, 9
3. Quinn, M. E. *et al., Chem. Abs.*, 1985, **102**, 208618

An unspecified sulfonation mass was being held at 160°C for 24 h to distil out water. After 22 h an exothermic reaction set in, and sulfur dioxide and sulfur trioxide were evolved in quantity. It was later found that catalytic impurities had reduced the decomposition temperature considerably [1]. The use of a bench scale heat flow calorimeter to determine safe operating limits for effective sulfonation (reaction unspecified) is described [2]. During start-up of a reactor for continuous sulfonation of an aromatic compound under conditions close to the region of high decompositional activity, a thermal explosion occurred in a pump and recirculation line. After full thermal investigation of the various contributory factors, it was concluded that the decomposition was too violent for emergency venting procedures to be effective, and alternative quenching and/or dumping systems were proposed [3].

Other sulfonation incidents will be found in the entries:
Chlorosulfuric acid, : Hydrocarbons, 3991
∗ 4-Hydroxy-3-nitrobenzenesulfonyl chloride, 2139

2-Methoxyanilinium nitrate, 2825
3-Nitrobenzenesulfonic acid, 2261
4-Nitrotoluene, 2760
Sulfuric acid, : Tetramethylbenzenes, 4473
See other GAS EVOLUTION INCIDENTS, UNIT PROCESS OR UNIT OPERATION INCIDENTS

SULFONIC ACID ESTERS RSO_2OR'

1. Collin, D. T. *et al., Chem. & Ind.*, 1987, 60
2. James, D. M., *Comprehensive Organic Chemistry*, Vol. 3, 342, Oxford, Pergamon, 1979
3. Dauben, W. G. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 3835
4. Anon., private comm., 1989

During the distillation at 81—89°C/0.8 mbar of cyclobutylmethyl methanesulfonate from a bath at 120°C, there was a sudden and violent explosion. Thermal instability of the ester was confirmed by heating a small sample at 0.5°C/min, when rapid autocatalytic and exothermic decomposition occurred at 110°C. In an isothermal test at 65°C a sample decomposed vigorously after 48 h. The decomposition involves rapid elimination of cyclopentene, the residue being methanesulfonic acid and polymer. Promotion of the decomposition by presence of added traces of methanesulfonic acid, and inhibition by the presence of sodium hydrogen carbonate confirms a mechanism involving acid catalysis. The ester is also unstable in toluene at 110°C, and in *N,N*-dimethylacetamide or sulfolane at 120°C. If the ester must be stored, this should be done as a 20 wt% solution in *tert*-butyl methyl ether at 0°C in presence of 5 mol% of sodium hydrogen carbonate. Cyclobutyl 4-toluenesulfonate, cyclopentylmethyl methanesulfonate and 1-pentyl methanesulfonate when heated at 0.5°C/min showed similar but slightly less energetic decomposition at 118, 128, and 185°C, respectively [1]. Instability of sulfonates of secondary alcohols is well documented [2]. A sample (25 g) of cyclobutylmethyl 4-toluenesulfonate was prepared by a literature method [3]. Upon attempted vacuum distillation at 0.27 mbar from a 50 ml flask in an oil bath at ca. 150°C, a violent explosion occurred. A sample from a repeat preparation was examined by DSC and at 2°C/min vigorous exothermic decomposition occurred at 140°C [4]. It is calculated that some 3.9 l of cyclopentene vapour at 140°C would cause a pressure surge to 80 bar in a 50 ml closed vessel.

Individually indexed compounds are:
Cyclobutyl 4-methylbenzenesulfonate, 3398
Cyclobutylmethyl methanesulfonate, 2510
Cyclopentylmethyl methanesulfonate, 2862
1-Pentyl methanesulfonate, 2545
See also SULFUR ESTERS

SULFONYL AZIDES RSO_2N_3

See ACYL AZIDES

SULFUR BLACK

Anon., *Ind. Eng. Chem.*, 1919, **11**, 892

Twenty-four hours after several barrels of the dyestuff were bulked, blended and repacked, spontaneous heating occurred. This was attributed to aerobic oxidation of excess sodium polysulfide used during manufacture.

See Sodium sulfide

See other SELF-HEATING AND IGNITION INCIDENTS

SULFUR COMPOUNDS

Groups and substances falling within this class are:

ALKANETHIOLS
ALKENEBIS(SULFONIUM PERCHLORATES)
ALLYL TRIFLUOROMETHANESULFONATES
ARENEDIAZO ARYL SULFIDES
BIS(ARENEDIAZO) SULFIDES
BIS(SULFUR)DIIMIDES
DIAZONIUM SULFATES
DIAZONIUM SULFIDES AND DERIVATIVES
METAL AMIDOSULFATES
METAL PHOSPHORUS TRISULFIDES
METAL SULFATES
METAL SULFIDES
NON-METAL SULFIDES
SULFONIC ACID ESTERS
SULFUR BLACK
SULFUR ESTERS
THIOPHENOXIDES
‘XANTHATES’

SULFUR ESTERS $RSOR'$, $RSO.OR'$, RSO_2OR'

The group name is intended to cover esters derived from sulfenic, sulfinic and sulfonic acids, some of which are thermally unstable. This is especially so for esters of unsaturated alcohols, which are also liable to polymerise, catalysed by the liberated acids. Individually indexed compounds are:

Allyl 4-toluenesulfonate, 3309
Allyl benzenesulfonate, 3149
Bis(trimethylsilyl) peroxomonosulfate, 2598
2-Buten-1-yl benzenesulfonate, 3310
3-Butyn-1-yl 4-toluenesulfonate, 3393
2-Chloro-2-propenyl trifluoromethanesulfonate, 1422
Cyclobutyl 4-methylbenzenesulfonate, 3398
Cyclobutylmethyl methanesulfonate, 2510
Cyclopentylmethyl methanesulfonate, 2862
Diallyl sulfate, 2437
Diethyl sulfate, 1704

Diethyl sulfite, 1703
1,10-Di(methanesulfonyloxy)deca-4,6-diyne, 3537
∗ Dimethyl selenate, 0926
† Dimethyl sulfate, 0925
Dimethyl sulfite, 0923
Ethyl 3,4-dihydroxybenzenesulfonate, 2983
Ethyl fluorosulfate, 0852
∗ 2-Isocyanoethyl benzenesulfonate, 3137
∗ *N*-Methyl-*p*-nitroanilinium 2(*N*-methyl-*N*-*p*-nitrophenylaminosulfonyl)ethylsulfate, 3707
1-Pentyl methanesulfonate, 2545
Prop-2-enyl trifluoromethanesulfonate, 1457
∗ Silyl trifluoromethanesulfonate, 0443
Trifluoroacetyl trifluoromethanesulfonate, 1054
3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2843
∗ Zinc ethylsulfinate, 1705
See ALLYL TRIFLUOROMETHANESULFONATES

SUNSPOTS

Ye, Y. *et al., Proc. 18th Int. Pyrotech. Semin.*, 1992, 1019

It is claimed that accidents in the Chinese pyrotechnic industry peak with the sunspot cycle.

SUPERHEATED LIQUIDS

1. Reid, R. C., *Superheated Liquids, A Laboratory Curiosity and, Possibly, an Industrial Curse, Chem. Eng. Educ.*, 1978, 60—63, 83—87; 108—111, 127—129; 194—196, 203—206
2. Reid, R. C., *Science*, 1979, **203**(4386), 1263—1365

This comprehensive survey of the title topic is in three parts, the first dealing with the theoretical background and laboratory studies, with 29 references. The second part, with 21 references deals with case histories and experimental studies of industrial vapour explosions. These involved the systems molten titanium—water, molten copper—water, molten aluminium—water, smelt—water, water—various cryogenic liquids, molten salt—water and molten uranium dioxide—liquid sodium. In the third part (with a further 26 references) is discussion of the various theories which abound, and the general conclusion that superheated liquids most likely play a major role in all these phenomena [1]. A further related publication covers BLEVEs and pressure let-down explosions [2].
See LIQUEFIED GASES, LIQUEFIED NATURAL GAS, MOLTEN METAL EXPLOSIONS, SMELT, VAPOUR EXPLOSIONS

SUPERIORS/SUPERVISORS

Can be a source of hazard. Some may react violently to suggestions that they are not omniscient. Suggested reactions should never be undertaken without investigating safety factors, not even if the editor is the superior in question.

SYNTHETIC PEROVSKITE OXIDES

Preparative hazard

Porta, P. *et al., J. Solid State Chem.*, 1999, **146**(2), 291; *Chem. Abs.*, 1999, **131**, 294667h

Mixed oxides of lanthanum copper and a third element from the first transition series were prepared by calcining what is described and abstracted as a citrate gel. The explosive nature of the reaction is noted. Inspection shows that the gel was a mixture of metal nitrate solution and citric acid, from which water had been evaporated.

See also METAL NITRATES

TETRAAZAMACROCYCLANEMETAL PERCHLORATES

Hung, Y., *Inorg. Synth.*, 1980, **20**, 112—113

The dichlorocobalt(IV) perchlorate salts complexed with [15] ane-N_4 and [16] ane-N_4 are described as potentially explosive.

See also AMMINEMETAL OXOSALTS, POLYAZACAGED METAL PERCHLORATES

TETRAHYDROPYRANYL ETHER DERIVATIVES

Meyers, A. I. *et al., Tetrahedron Lett.*, 1976, 2417—2418

The tetrahydropyranyl group, commonly used in synthetic procedures to protect hydroxyl groups, appears not to be safe when peroxidising reagents are used with tetrahydropyranyl ether derivatives, because explosive peroxides, not destroyed by the usual reagents, are produced.

The hydroboration product of 2-methyl-2-propenyl tetrahydropyranyl ether was routinely oxidised with alkaline hydrogen peroxide, then treated with sodium sulfite solution during work-up. The product gave a negative test for peroxides but exploded violently during attempted distillation at 0.06 mbar from a vessel at 120°C. Epoxidation of 3-methyl-3-butenyl tetrahydropyranyl ether with peroxyacetic acid gave, after sulfite treatment, an apparently peroxide-free product. However, after distillation at 1 mbar, the fore-run (b.p. 40—70°C) exploded violently when the flask was disturbed. The main fractions were found subsequently to give strong positive indications for the presence of peroxides which were only removed after prolonged treatment with sodium thiosulfate. (There is some evidence to suggest that sodium sulfite may under certain circumstances actually promote peroxide formation.)

Other acetal-type protecting groups (tetrahydrofurfuryl ethers, methoxymethyl ethers, 1,3-dioxolanes) are also considered to be incompatible with oxidising agents.

See other PEROXIDISABLE COMPOUNDS

TETRA(N-METHYLPYRIDYL)PORPHINE PERCHLORATES

Reid, J. B. *et al., Inorg. Chem.*, 1977, **16**, 968

Variously metallated derivatives of the porphine nitrate were converted to the perchlorate salts, but several exploded during drying. The need for great caution in attempting to prepare the anhydrous perchlorates is stressed.

See Tetrakis(4-*N*-methylpyridinio)porphinecobalt(III)(5+) perchlorate

See other AMMINEMETAL OXOSALTS

TETRAMETHYL [14] TETRAENE-N_8 METAL PERCHLORATES

Peng, S.-M. *et al., Inorg. Chem.*, 1978, **17**, 120

The perchlorate salts of the complexes with divalent cobalt, nickel, and particularly iron are potentially explosive, and storage for more than 4 weeks is not advised.

See AMMINEMETAL OXOSALTS, [14] DIENE-N_4 COMPLEXES

TETRAZENES $R_2NN{=}NNR_2$

Houben Weyl, 1967, 10/2, 828

Several compounds of this class explode forcefully on heating, the tetramethyl and tetraallyl derivatives are specifically mentioned.

Individual compounds are:

1-Acetyl-4-(4′-sulfophenyl-3-tetrazene, 2977
1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate, 2582
3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2800
Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2249
Tetraallyl-2-tetrazene, 3539
Tetramethyl-2-tetrazene, 1753

See HIGH NITROGEN COMPOUNDS

TETRAZOLES

1. Benson, F. R., *Chem. Rev.*, 1947, **41**, 4—5
2. Morisson, H., *Util. Elem. Pyrotech. Explos. Syst. Spatiaux, Colloq. Int. 1968* (publ. 1969), 111—120
3. Schroeder, M. A., *Rept. AD-A018652*, Richmond (Va.), USNTIS, 1975
4. Grimmett, M. R.; *Barton & Ollis*, 1979, Vol. 4, 364
5. Matsuzawa, T. *et al., Loss Prevention and Safety Promotion in the Process Industries*, (Mewis, Pasman and De Rademaker: Eds), Vol II, 315, Amsterdam, Elsevier, 1995

There is a wide variation in thermal stability in derivatives of this high-nitrogen nucleus, and several show explosive properties [1]. The characteristics of explosive tetrazole salts have been summarised [2], and the relationship between structure and reactivity of isomeric 1- and 2-tetrazole derivatives has been reviewd in a ballistics context [3]. It is claimed that tetrazole diazonium salts detonate, in water, at concentrations little above 2%, at 0°C [4]. A sensitivity study has been made of numerous tetrazoles, their salts, and compositions thereof with oxidants, as gas generators for airbags. Salts are less sensitive than the parent tetrazoles. Mixtures with potassium perchlorate are both more energetic and more sensitive, those with potassium nitrate are usually similar, though some are less sensitive to electric discharge. In the absence of oxidants, hydrogen cyanide is a frequent decomposition product [5]. Individually indexed compounds are:

5-Amino-2-ethyl-2*H*-tetrazole, 1264
5-Aminotetrazole, 0460
5-Azidotetrazole, 0387
Barium 5,5′-azotetrazolide, 0574
1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene, 0823

N-Chloro-5-phenyltetrazole, 2670
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1425
5-Cyano-2-methyltetrazole, 1117
2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate, 0970
1,3-Di(5-tetrazolyl)triazene, 0774
5-(Diazomethylazo)tetrazole, 0715
5-Diazoniotetrazolide, 0545
1-Dichloroaminotetrazole, 0370
1,2-Dihydropyrido[2,1-*e*]tetrazole, 1828
5-(4-Dimethylaminobenzeneazo)tetrazole, 3156
Disodium 5,5′-azotetrazolide, 1014
* Disodium 5,5′-azoxytetrazolide, 1015
Disodium 5-tetrazolazocarboxylate, 1008
Disodium tetrazole-5-diazoate, 0546
Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2352
2-Ethyltetrazole, 1209
5-Ethyltetrazole, 1210
5,5′-Hydrazotetrazole, 0822
Lead 5,5′-azotetrazolide, 1016
Mercury 5,5′-azotetrazolide, 0976
Mercury(II) 5-nitrotetrazolide, 0977
2-Methyl-5-vinyltetrazole, 1508
2-Methyltetrazole, 0810
1-(2-Naphthyl)-3-(5-tetrazolyl)triazene, 3388
5-Nitro-2-picryltetrazole, 2634
5-*N*-Nitroaminotetrazole, 0414
1-(2-Nitrophenyl)-5-phenyltetrazole, 3596
5-Nitrotetrazole, 0386
* Pentazole, 4437
3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2800
5-Phenyltetrazole, 2723
Potassium 1-tetrazolacetate, 1103
Silver 1,3-di(5-tetrazolyl)triazenide, 0686
Silver 5-aminotetrazolide, 0391
Silver tetrazolide, 0365
Sodium 1-tetrazolacetate, 1116
Sodium 5(5′-hydroxytetrazol-3′-ylazo)tetrazolide, 0678
Sodium 5-azidotetrazolide, 0548
Sodium 5-(dinitromethyl)tetrazolide, 0677
Sodium 5-nitrotetrazolide, 0544
1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene, 3008
Tetrazole, 0410
Tetrazole-5-diazonium chloride, 0369
5-Trichloromethyl-1-trimethylsilyltetrazole, 1921
5-Trichloromethyltetrazole, 0653
See other HIGH-NITROGEN COMPOUNDS

TEXTILE CLOTHING STATIC CHARGES

Wilson, N., *J. Electrost.*, 1977, **4**, 67—84

The clothing worn by a process operator insulated from earth may develop static charges far higher (up to 100-fold) than the minimum ignition energies for various flammable gas—air mixtures. This is true for a wide range of clothing materials including cotton. Dangerous levels of charge may be avoided by ensuring a low resistivity of the surface material worn outermost.

See other IGNITION SOURCES

THEORY WITHOUT DETAILED THOUGHT

Hooton, K., *Chem. Brit.*, 2000, **36**(9), 21

An anecdote is told of a student who, reasoning from Le Chatelier's Principle, reacted to a warning that hydrogen peroxide evolved oxygen by screwing down the cap of a bottle especially firmly for pressure to drive the reaction into reverse. The logic is impeccable, somewhere well short of the interior of neutron stars water, oxygen and hydrogen peroxide must establish equilibrium. But it is at no pressure that common terrestrial construction materials will resist – result explosion. Other Principles may also yield hazardous practice, the devilment is, as ever, in the detail.

THERMAL EXPLOSIONS

Verhoeff, J., *Experimental Study of the Thermal Explosion of Liquids*, Doctoral Thesis, University of Delft, 1983

In a study of the course of thermal explosions in low, high and constant pressure autoclave experiments, 3 stages of thermal runaway, initiation and explosion were identified and studied in detail. Most of the work was done with *tert*-butyl peroxybenzoate, but limited comparative examinations were carried out on 8 other energetic substances.

THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

1. Grewer, T., *Chem. Ing. Tech.*, 1975, **47**, 230—235
2. Hartgerink, J. W., *Proc. 3rd Symp. Chem. Probl. Connected Stab. Explos.* 1973, (publ. 1974), 220—230
3. Grewer, T., *Chem. Abs.*, 1980, **93**, 210923
4. Tyler, B. J., *Chem. Brit.*, 1981, **17**, 274, 276
5. O'Brien, G. J., *Chem. Eng. Progr.*, 1982, 78(1), 46—49
6. Fierz, H. *et al., Chem. Engr.*, 1984, **400**, 9—10
7. Gibson, N., *Chem. & Ind.*, 1984, 209—211
8. Smith C. D., *Chem. Eng. Progress*, 1994, **90**(9), 67

The importance of gaining knowledge on the reaction parameters of exothermic reaction systems to assess potential processing hazards is discussed in detail. The roles of DTA, adiabatic storage tests and adiabatic reaction tests were discussed, and suitable techniques described with reference to practical examples of thermally unstable systems [1]. Two storage tests (adiabatic storage and isothermal heat generation) were described which give information on the induction period of instability.

An exothermal decomposition meter, with 100-fold higher sensitivity than DTA is described [2]. The importance of the relationship between reaction energy and reaction rate for batch reactions, and of the factors which may lead to reaction delays and instability, and of secondary reactions, are discussed and exemplified [3].

The safety margin between reaction stability and runaway may be as little as 10—20°C, and this may be diminished or eliminated by apparently minor changes (higher initial temperature or concentration, better catalysts, less stirring or cooling capacity) in processing conditions [4]. A standardised review procedure to identify and eliminate factors likely to lead to reaction instability is described [5]. Application of the bench scale heat flow calorimeter to the overall problems of ensuring stability in chemical processing operations is discussed with examples [6]. The advantages to be gained by using a range of tests to identify potential processing hazards are outlined [7]. Considerations of explosion and detonation are expounded. A quick simple scanning procedure for detecting self-heating to explosion is detailed, much cheaper than Accelerating Rate Calorimetry. There is also a test for transition from deflagration to detonation (though this will only detect materials of greater detonability than most explosives) [8].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

THERMITE REACTIONS

1. Bond, 1991, 63
2. Gibson, N. *et al., Proc. 3rd Symp. Chem. Proc. Haz. Ref. Plant Des.*, 26—35, London, IChE, 1968
3. Britten, G. C., *School Sci. Rev.*, 1976, **57**(201), 732
4. Hadfield, J. M., *School Sci. Rev.*, 1980, **62**(219), 394
5. Bozzelli, J. W. *et al., J. Chem. Educ.*, 1979, **54**, 675—676
6. Roebuck, P. J., *Educ. Chem.*, 1979, **16**, 178—179
7. Ivanov, G. V. *et al., Chem. Abs.*, 1979, **91**, 76323
8. Billinge, K., *Fire Prev. Sci. Technol.*, 1981, (24), 13—19
9. Shidlovskii, A. A. *et al., Chem. Abs.*, 1983, **98**, 18942
10. Eastland, G. W., *J. Chem. Educ.*, 1984, **61**, 723
11. Zumdahl, S. S., *Chem. Eng. News*, 1990, **68**(20), 2
12. Fawcett, H. *et al., CHAS Notes*, 1990, **VIII**(3), 2
13. Ismailov, M. B., *et al., Fizika Goreniya i Vzryva*, 1992, **28**(1), 46
14. Filatov, B. M., *et al., ibid.* 53
15. Wright, S. W., *J. Chem. Educ.*, 1994, **71**(3), 251

The name given to reaction of a very electropositive metal with the oxide of a less active one, producing the less electropositive metal, usually incandescent. Archetypally a reaction between aluminium and iron oxide, now applied to a variety of similar combinations. Thermite reactions of rusty iron falling on other metals, especially magnesium protective electrodes, are a source of ignition of fires on oil tankers. Aluminium paint is only a danger if it has previously been to 150°C, the risk remains on cooling, bulk aluminium and alloys do spark fires, as can titanium [1]. The conditions under which incendive sparks are generated by impact of a striker with an aluminium smear on rusted steel were investigated. This was part of a comprehensive series of experiments to assess the importance of the variables and the mechanism of the process which leads to ignition of flammable materials in chemical plant environments [2]. Further to an earlier publication on the use of transition metal oxides in school demonstrations of thermite reactions [3], it was stressed that use of manganese dioxide with aluminium may lead to explosion [4]. The use of potassium permanganate—glycerol mixture to ignite thermite mixture is more reliable than the magnesium ribbon/barium oxide:aluminium igniter [5].

Safety aspects are detailed for practical demonstrations of thermite reactions of aluminium with various oxides of chromium, cobalt, copper, iron, manganese, and nickel. The molar heat of reaction is maximal for Fe_3O_4, but the exotherm on a weight basis is maximal for the stoicheiometric mixture with MnO_2 at 4.8 kJ/g [6]. The dependence of the burning rate on pressure (1—80 kbar) was studied for mixtures of magnesium, zinc or zirconium with barium dioxide, chromium(III) oxide, iron(III) oxide, manganese dioxide, molyybdenum trioxide, lead dioxide or vanadium pentoxide [7]. Combustion mechanisms for aluminium thermites with chromium(III) and Ni(II) oxides, also with silica, have been studied [12]. Five incidents in a survey of frictional ignition hazards probably involved thermite reactions [8], and the combustion rate of nickel oxide—aluminium mixtures is 2.5-fold greater than iron oxide mixtures [9]. Precautions necessary to activate large-scale (6 kg of mixture!) spectacular demonstrations are detailed [10]. Caution is given against conducting thermite demonstrations over water, or wet sand, after a lecture/demonstration audience were showered with hot iron [11]. A second-hand report of what is almost certainly the same incident claims that the front row of seats was pulverised — tales seldom lessen in the telling. Not only metal oxides but some halides undergo thermite type reactions with aluminium or magnesium [13]. Individually indexed examples are:
Aluminium, : Metal oxides, etc., 0048
Aluminium, : Sodium sulfate, 0048
Aluminium—magnesium alloy, : Iron(III) oxide, Water, 0053
Calcium acetylide, : Iron(III) chloride, Iron(III) oxide, 0582
Copper(I) oxide, : Aluminium, 4282
Iron(II,III) oxide, : Aluminium, Sulfur, 4399
Magnesium, : Metal oxides, 4685
Magnesium, : Metal oxosalts, 4685
Magnesium, : Rusty steel, 4685
Manganese(IV) oxide, : Aluminium, 4700
See also VAPOUR EXPLOSIONS
See other REDOX REACTIONS

THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

1. Grewer, T. *et al., Proc. 4th Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, A1—A11, Rugby, IChE, 1983
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
3. *Thermal Hazards of Chemical Reactions*, Grewer, T., Amsterdam, Elsevier (Industrial Safety Series, Vol. 4), 1994.
4. Chervin, S. *et al., Process Safety Progress*, 2003, **22**(4), 242

The difficulties in relating the calculated thermodynamic energy of decomposition (—ΔU) to that occurring in practice are discussed, and values of the experimentally observed energies of decomposition for some characteristic molecular structures are tabulated in comparison with the calculated values. A second table gives the range of decomposition energies which have been measured by DSC for 10 series of compounds each containing the same characteristic molecular structural group(s). These values are:— nitro, 220—410 kJ/mol (in 30 nitro compounds, with dinitro towards the top of the range); nitroso, 90—290 (4); oxime, 170—230 (2); isocyanate, 20—30 (3); azo, 100—180 (5); hydrazo, 65—80 (3); diazonium, 130—165 (5); peroxide, 200—340 (20); epoxide,4 5—80 (3); double bond, 40—90 (6). The reasons for the observed variation in these energies of decomposition are discussed [1].

The relationships between energy of decomposition and processing hazards are then considered, and the practical importance of using values of energy released per unit mass, rather than on a molar basis is stressed, and the decomposition energies in J/g are given in a further table. Finally it is suggested that in ‘open vessel’ processes (with man-hole sized opening), substances with exothermic decomposition energies below 500 J/g are not likely to be hazardous, but that in ‘closed vessel’ processes (opening is a safety valve or bursting disk), an upper limit of 150 J/g might be appropriate [1]. (Some of the alkali chlorate decomposition explosions experienced in, effectively open, bulk storage must have been of lower energy than 500 J/g – Editor’s comment.)

In a comprehensive investigation of exothermic decomposition, the thermal behaviour of a further 105 reactive componds (included below) in 18 classes was investigated by DSC, and the heats of decomposition so determined were tabulated. Of these compounds, 39, together with 21 other compounds, were investigated in detail in a series of adiabatic Dewar tests to examine the relationship between adiabatic temperature and induction time to exothermic decomposition. The adiabatic holding temperature which gives a time to exothermic decomposition of 24 hours has been proposed as a new practical characteristic for the particular compound. This temperature ‘T_{ait24}’ can be calculated from isothermal DTA diagrams [2], and this temperature is given in the text entries in this volume for the 60 compounds investigated. Grewer’s work has subsequently produced a more widely available publication [3]. Other authors have produced a tabulation of energies and decomposition onset temperatures for functional groups, both those representing the energy and others facilitating decomposition [4].

Some other examples may be found in the entries:

Acetohydrazide, 0908
Acetone oxime, 1254
Acetylenedicarboxylic acid, 1401
† Acrylaldehyde, 1142
† Allyl acetate, 1906
N-Allylthiourea, 1595
4-Aminophenylazobenzene, 3481
Ammonium dichromate, 4240
Ammonium peroxodisulfate, 4571
2-Azido-2-phenylpropane, 3154

4-Azidobenzaldehyde, 2693
† Aziridine, 0859
Azobenzene, 3477
Azoformamide, 0812
Azoxybenzene, 3479
Benzaldehyde oxime, 2756
Benzyl chloride, 2734
4-Bromoaniline, 2289
2-Bromocyclohexanone, 2386
Butane-2,3-dione dioxime, 1590
† Butyl isocyanate, 1925
4-Chloro-1,2-benzenediamine, 2340
4-Chloro-1,3-benzenediamine, 2341
† 1-Chloro-2,3-epoxypropane, 1158
1-Chloro-2,4-dinitrobenzene, 2091
4-Chloro-2,6-diamino-*N*-methylaniline, 2818
4-Chloro-2-aminophenol, 2296
3-Chloro-4-methoxyaniline, 2791
Chloroacetamide, 0784
3-Chloroaniline, 2294
2-Chloroaniline, 2293
4-Chloroaniline, 2295
2-Chloronitrobenzene, 2134
4-Chloronitrobenzene, 2135
2(3-Chlorophenoxy)ethylamine, 2971
N-Chlorosuccinimide, 1423
N-Chlorotoluene-4-sulfonamide, 2793
Dibenzoyl peroxide, 3632
2,4-Dibromoaniline, 2219
2,3-Dichloroaniline, 2230
2,4-Dichloroaniline, 2231
2,5-Dichloroaniline, 2232
3,4-Dichloroaniline, 2234
N,N-Dichlorobenzenesulfonamide, 2237
2,4-Dimethoxyaniline, 2993
3,5-Dimethoxyaniline, 2994
Dimethyl acetylenedicarboxylate, 2333
† Dimethyl sulfoxide, 0917
N,N-Dimethyl-2-chloroacetamide, 1580
N,N-Dimethyl-4-nitrosoaniline, 2975
† 1,1-Dimethylhydrazine, 0950
3,5-Dinitro-2-toluamide, 2936
2,4-Dinitroaniline, 2270
1,3-Dinitrobenzene, 2188
2,4-Dinitrophenol, 2190
2,4-Dinitrotoluene, 2722

† 1,4-Dioxane, 1612
1,2-Diphenylhydrazine, 3511
1,1-Diphenylhydrazinium chloride, 3513
1,3-Diphenyltriazene, 3500
2,3-Epoxypropanol, 1225
† Ethylene oxide, 0825
Fumaric acid, 1442
Fumarodinitrile, 1393
Glucose, 2513
Glutarodinitrile, 1864
Hydroxylaminium sulfate, 4570
N-Hydroxysuccinimide, 1465
Maleic anhydride, 1400
Maleimide, 1414
Malononitrile, 1075
4-Methoxy-1,3-phenylenediamine, 2822
2-Methoxyaniline, 2812
3-Methoxyaniline, 2813
4-Methoxyaniline, 2814
3-Methoxybenzylamine, 2992
† 2-Methoxyethylamine, 1308
3-Methoxypropylamine, 1724
1-Naphthyl isocyanate, 3384
2-Nitroaniline, 2306
3-Nitroaniline, 2307
4-Nitroaniline, 2308
4-Nitrobenzaldehyde, 2684
2-Nitrobenzaldehyde, 2682
3-Nitrobenzaldehyde, 2683
Nitrobenzene, 2255
3-Nitrobenzoic acid, 2690
4-Nitrobenzoic acid, 2691
2-Nitrobenzoic acid, 2689
4-Nitrobenzyl chloride, 2710
4-Nitrodiphenyl ether, 3465
4-Nitrophenol, 2260
3-Nitrophenol, 2259
2-Nitrophenol, 2258
1-Nitroso-2-naphthol, 3244
Nitrosobenzene, 2254
N-Nitrosodiphenylamine, 3480
2-Nitrosophenol (1,2-Benzoquinone monoxime), 2256
4-Nitrosophenol (1,4-Benzoquinone monoxime), 2257
2-Nitrotoluene, 2759
4-Nitrotoluene, 2760
3-Phenoxy-1,2-epoxypropane, 3144

Phenyl azide, 2264
Phenyl isocyanate, 2681
2-Phenylethyl isocyanate, 3133
Phenylhydrazine, 2366
Poly(vinyl alcohol), 0827
Potassium hydrogen acetylenedicarboxylate, 1378
Potassium peroxodisulfate, 4663
† 2-Propen-1-ol, 1219
† Propylene oxide, 1221
Pyridine *N*-oxide, 1843
Sodium 3-nitrobenzenesulfonate, 2177
Sodium azide, 4753
Sodium chloroacetate, 0690
Sodium methoxide, 0463
Sodium peroxodisulfate, 4803
Sodium trichloroacetate, 0605
Styrene, 2940
Sucrose, 3552
1,2,4-Triazole, 0765
2,3,4-Trichloroaniline, 2156
Trimethylamine oxide, 1309
2,4,6-Trinitrotoluene, 2697
See CALORIMETRY, CELLULOSE, THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS
See also EXOTHERMICITY

THIATRIAZOLES

1. Banert, K. *et al., Tet. Lett.*, 2001, **42**(35) 6133
2. Holm. A., *Comprehensive Heterocyclic Chemistry*, (Ed. Katritzky, A. R.), Vol. 6, Pt 4B, Oxford, Pergamon, 1984

The paper warns that isolated examples of the 1,2,3,4-thiatriazoles are explosive. It starts from the chloro-compound and proceeds thence to allyl and propargyl ethers. The latter, especially, have an additional source of explosive instability [1]. Aminothiatriazoles are reported to explode on melting [2]. 1,2,3,4-thiatriazole-5-thio derivatives are the actual structure of the, generally explosive, 'azidodithioformic', or 'azidodithiocarbonic' compounds. It seems probable that the 5-oxy compounds are also hazardous, if isolable. There is no immediate reason to suppose the less known 1,2,3,5 thiatriazole system would be much more stable.

Azidodithioformic acid, 0385
5-Chloro-1,2,3-thiadiazole, 0651
HIGH-NITROGEN COMPOUNDS
N—S COMPOUNDS

THIONOESTERS

1. Andreozzi, R. *et al., J. Loss Prev.*, 1999, **12**, 315
2. Andreozzi, R *et al., J. Haz. Mat.*, 1999, **64**(3), 283

Sulfur forms double bonds less readily than does oxygen and materials containing these are correspondingly less stable. Thus trimerisation of thioaldehydes is not a hazard (unlike the smaller oxygen analogues) since it is virtually impossible to isolate the monomers in the first place. Thionoesters are, however, tolerably stable at room temperature. On heating, they are subject to various intramolecular reactions which exchange the double and singly bonded status of the sulfur and oxygen atoms; these are significantly exothermic. Where possible, elimination of olefins has the lower activation energy and may generate gas. If this is not possible, isomerisation to the corresponding =O ester will take place. The isomerisation may produce about 100 kJ/mole.On a small laboratory scale there will be no problem, but uncontrollable runaways leading to loss of containment and fire have been observed in pesticide manufacture and formulation, thionophosphate groups being common in insecticides. Should less sensitive, but higher energy groups, such as nitro- also be present, the thione rearrangement may act as a trigger to these, this has been experienced in parathion manufacture. The potential problem is not limited to the thionophosphates of the references above, it can be observed in decomposition/rearrangement of O-alkyl, or aryl, xanthates and is doubtless general.

See Diethyl 4-nitrophenyl thionophosphate

THIOPHENOXIDES **ArS^-**

Diazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 9)

THORIUM FURNACE RESIDUES

Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163

Many furnace residues (fine powders and salts) deposited in the upper parts of furnaces used for thorium melting operations, are highly pyrophoric and often ignite as the furnace is opened. Such residues may be rendered safe by storage under water for 60—90 days. If the water is drained off early, ignition may occur.

See other PYROPHORIC MATERIALS

TOLLENS' REAGENT

1. Green, E., *Chem. & Ind.*, 1965, 943
2. Waldman, H., *Chimia*, 1959, **13**, 297—298
3. Coltoff, W., *Chem. Weekblad*, 1932, **29**, 737
4. MCA Guide, 1972, 319
5. Breedlove, C. H. *et al., J. Coll. Sci. Teach.*, 1983, **12**, 281
6. Klinger, G. S., *et al., Chem. Eng. News* 1996, **74**(2), 2
7. http//news.bbc.co.uk/go/pr/fr/-/hi/england/tyne/3083899.stm

This mixture of ammoniacal silver oxide and sodium hydroxide solution is potentially dangerous, because if kept for a few hours it deposits an explosive precipitate. This danger was described by Tollens in 1882 but is not generally known now. Prepare the reagent just before use, in the tube to be used for the test, and discard immediately after use, **NOT** into a container for silver residues [1]. Several earlier references to hazards of storing the reagent before or after use are discussed [2]. On one occasion a violent explosion of the reagent occurred 1 h after preparation and before a precipitate had formed [3], and on another, an empty but unrinsed test tube exploded when picked up [4]. Attempts to recover silver from a batch of the reagent of indeterminate age (!) caused explosions [5]. One hundred and twenty years on, pre-prepared Tollens reagent is still causing explosions [6].

See FULMINATING METALS, SILVERING SOLUTIONS

TOXIC HAZARDS

Toxic hazards have been specifically excluded from consideration in this Handbook, with the very limited exception of volatile toxic products of reactions which might be unexpected to the average chemistry graduate. But poisoning risks are at least as important as reactive ones, and particularly on a long-term basis. Due account of toxic hazards must therefore be taken in planning and executing laboratory work, particularly if unfamiliar materials are being brought into use.

It is perhaps appropriate to point out that many of the elements or compounds listed in this Handbook are here because of a high degree of reactivity towards other materials. It may therefore broadly be anticipated that under suitable circumstances of contact with animal organisms (including readers), a high degree of interaction will ensue, with possible subsequent onset of toxic or other deleterious effects.

See APROTIC SOLVENTS

TRIALKYLALUMINIUMS R_3Al

Basyrov, Z. B. *et al.,Chem. Abs.*, 1988, **109**, 215294

In a review of the fire and explosibility hazards of this group, data on 15—50% solutions of trimethyl- and triisobutyl-aluminium in isopentane and in hexane are given.

A highly reactive group of compounds, of which the lower members are extremely pyrophoric, with very short ignition delays of use in rocket- or jet-fuel ignition systems. Storage stability is generally high (decomposition with alkene and hydrogen evolution begins above about 170—180°C), but branched alkylaluminiums (notably triisobutylaluminium) decompose above 50°C. Individually indexed compounds, many commercially available in bulk, are:

3-Buten-1-ynyldiethylaluminium, 3012
3-Buten-1-ynyldiisobutylaluminium, 3543
∗ Diethyl-3-diethylaminopropylaluminium, 3408
† Triethylaluminium, 2548
† Triisobutylaluminium, 3562
Triisopropylaluminium, 3208
Trimethylaluminium, 1287
Tripropylaluminium, 3209
∗ Tris(trimethylsilylmethyl)aluminium, 3578
∗ Tris(trimethylsilylmethyl)indium, 3579

TRIALKYLANTIMONY HALIDES R_3SbX

Leleu, *Cahiers*, 1977, (88), 361

These ignite spontaneously in air.

See other ALKYLMETAL HALIDES

TRIALKYLBISMUTHS R_3Bi

Oxidants

Gilman, H. *et al., Chem. Rev.*, 1942, **30**, 291

The lower alkylbismuths ignite in air, and explode in contact with oxygen, or conc. nitric or sulfuric acids. Individually indexed compounds are:

Tributylbismuth, 3565
Triethylbismuth, 2556
* Trivinylbismuth, 2385

See other ALKYLMETALS

TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES $R_3SiOPbR'_3$

Houben-Weyl, 1975, Vol. 13.7, 118

Compounds containing Si—O—Pb bonds may interact explosively with oxygen at about 140°C, or with aluminium chlorides, acyl halides or anhydrides.

See related ALKYLMETALS, ALKYLNON-METALS

TRIAZENES $RN{=}N{-}NR'R''$

1. Houben Weyl, 1967, 10/2, 827
2. Houben-Weyl, 1965, Vol. 10.3, 700, 717, 722, 731
3. Vaughan, K. *et al., Chem. Soc. Rev.*, 1978, **7**, 378—379
4. White, E. H. *et al., Org. Synth.*, 1973, Coll. Vol. 5, 797
5. Rondevstedt, C. S. *et al., J. Org. Chem.*, 1957, **22**, 200

Care is required with these compounds since many explode on heating [1]. A number of triazene derivatives bearing hydrogen, or cyano, hydroxy or nitroso groups on the terminal nitrogen of the chain are unstable, mainly to heat [2]. Purification of triazenes by vacuum sublimation carries the risk of explosion [3]. Further examples of unstable triazenes and precautions are given [4,5].

Individually indexed compounds are:

* 1-Acetyl-4-(4′-sulfophenyl)-3-tetrazene, 2977
1-Benzyl-3-(4-tolyl)triazene, 3650
1,3-Bis(phenyltriazeno)benzene, 3751
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1425
1,3-Di(5-tetrazolyl)triazene, 0774
3,3-Dimethyl-1-(3-quinolyl)triazene, 3392
3,3-Dimethyl-1-phenyltriazene, 2991
1,3-Dimethyltriazene, 0941
* 1,5-Diphenylpentaazadiene, 3501
1,3-Diphenyltriazene, 3500
3-Ethyl-1(4-methylphenyl)triazene, 3165

1-(4-Methoxyphenyl)-3-methyltriazene, 2995
1-(2-Naphthyl)-3-(5-tetrazolyl)triazene, 3388
1-Phenyl-3-*tert*-butyltriazene, 3329
N-Phenylazopiperidine, 3401
Silver 1,3-di(5-tetrazolyl)triazenide, 0686
Silver 3-cyano-1-phenyltriazen-3-ide, 2666
3-HYDROXYTRIAZENES
3-NITROSOTRIAZENES
See 3-CYANOTRIAZENES
See other HIGH-NITROGEN COMPOUNDS

TRIAZOLES

1. Wilson, W. S. *et al., Austr. J. Chem.*, 1992, **45**(3), 513, 525
2. Grimmett, M. R.; *Barton & Ollis*, 1979, Vol. 4, 364

For a study of nitrophenylbenzotriazoles as explosives, the triazole ring conferring impact sensitivity, see [1]. Simpler nitro- and azido- triazoles also find explosive use. On heating to above 260°C, 1,2,3-triazole halides explode violently [2]. Several examples of instability among this group of relatively high-nitrogen compounds may be found under the entries:

5-Amino-3-phenyl-1,2,4-triazole, 2947
4-Amino-4*H*-1,2,4-triazole, 0808
Ammonium 3,5-dinitro-1,2,4-triazolide, 0819
3-Azido-1,2,4-triazole, 0713
3,3'-Azo-(1-nitro-1,2,4-triazole), 1397
Benzotriazole, 2262
Bis(1-benzo[*d*]triazolyl) carbonate, 3592
Bis(1-benzo[*d*]triazolyl) oxalate, 3622
* Bis(1-methylbenzotriazole)cobalt(II) nitrate, 3645
1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene, 1571
N-Chloro-4,5-dimethyltriazole, 1486
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1341
4-Diazo-1,2,3-triazole, 0674
3-Diazo-3*H*-1,2,4-triazole, 0673
4-Diazo-5-phenyl-1,2,3-triazole, 2905
3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2904
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1847
* 5-Hydrazino-1,2,3,4-thiatriazole, 0461
1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0813
4-Hydroxy-3,5-dimethyl-1,2,4-triazole, 1570
1-Hydroxybenzotriazole, 2265
* 5-Methoxy-1,2,3,4-thiatriazole, 0769
1-Methyl-1,2,3-triazole, 1185
3-Nitro-1,2,4-triazolone, 0712
4-Nitro-1-picryl-1,2,3-triazole, 2881
4-Nitroamino-1,2,4-triazole, 0773

4,6- or 5,6- or 5,7-Dinitro-1-picrylbenzotriazoles, 3432
1-Picryl-1,2,3-triazole, 2893
Silver benzo-1,2,3-triazole-1-oxide, 2120
1,2,3-Triazole, 0764
1,2,4-Triazole, 0765
1,2,4-Triazole-3-diazonium nitrate, 0676
See other HIGH-NITROGEN COMPOUNDS

TRICARBONYL(CYCLOPENTADIENYL)SILYLMETAL COMPLEXES

Hagen, A. P. *et al., Inorg. Synth.*, 1972, **17**, 104

During the preparation of the complexes of chromium, molybdenum and tungsten from K[M(CO)$_3$C$_5$H$_5$] and bromosilane, the residues from sublimation of the products are all pyrophoric.

See related CARBONYLMETALS, ORGANOMETALLICS

N,N,N′-TRIFLUOROAMIDINES —C(NF)NF$_2$

Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3093

This group of compounds, (which combines the structural features of both the separately treated N-HALOIMIDES and DIFLUOROAMINO COMPOUNDS, each of high reactivity) is explosively unstable.

All the N—F compounds involved in the synthesis of a group of C$_3$—C$_7$ *N*-trifluoroalkylamidines were shock-sensitive explosives in varying degrees. Several were only stable in solution, and others exploded during analytical combustion. Individually indexed compounds are:

2-Chloro-*N,N,N′*-trifluoropropionamidine, 1125
Decafluorobutyramidine, 1367
* Pentafluoroguanidine, 0358
Perfluoro-1-aminomethylguanidine, 0643
Perfluoroformamidine, 0349
N,N,N′-Trifluorohexanamidine, 2442
N,N,N′-Trifluoropropionamidine, 1168
See other N-HALOGEN COMPOUNDS

TRIFLUOROMETHYLBORANES

Michl, J. *et al., J. Amer. Chem. Soc.*, 2000. **122**, 10255

A chemically unreactive, but friction sensitive explosive, caesium dodecakis(trifluoromethyl)carba-*closo*-dodecaborate was prepared. Explosive products have also resulted from attempts to prepare the corresponding dicarbododecaborane. The explosion reaction appears to involve formation of boron trifluoride and graphite, and may therefore be more general.

See other BORANES

TRINITROETHYL ORTHOESTERS $HC[OCH_2C(NO_2)_3]_3$, $C[OCH_2(NO_2)_3]_4$

Nitromethane

Shimio, K. *et al., Chem. Abs.*, 1976, **85**, 194924

Both tris(2,2,2-trinitroethyl)orthoformate and tetrakis(2,2,2-trinitroethyl)-orthocarbonate form powerfully explosive solutions in nitromethane. The oxygen balance of the esters are +154 and +182%, respectively. The compounds are:

Tetrakis(2,2,2-trinitroethyl)orthocarbonate, 3126

Tris(2,2,2-trinitroethyl) orthoformate, 2782

See OXYGEN BALANCE, POLYNITROALKYL COMPOUNDS

TRIPHENYLMETHYL CHLORIDES Ar_3CCl

Anon., 2003

Tritylation of some compounds of low thermal stability increases neither the kinetic nor thermodynamic stability, measured decomposition enthalpies per gram remaining high. Possibly the energy theoretically represented by the three benzene rings in the trityl group makes itself apparent.

Preparative Hazard

Editor's experience

One synthesis of this class is by reaction of a benzotrichloride with an aromatic substrate (usually employed in small excess as the solvent) with aluminium chloride as the nominal catalyst. Part way into the reaction, a second liquid phase separates, this is substantially ionic and permits accelerated reaction. At the same time, hydrogen chloride evolution will increase, often leading to pressurisation. Some examples also show crystallisation of the trityl tetrachloroaluminate, which may further encourage gas evolution.

Preparation from the triphenylmethanol, by reaction with sulfinyl chloride, also often gives problems of pressurisation, associated with the appearance, and then reaction, of an aqueous phase.

See PHASE CHANGES

TURPENTINE

NSC 367, 1968;
HCS 1980, 948

Paulin, M. S., *Tappi J.*, 1983, **66**(4), 91—92

A 45 kl tank of sulfate turpentine from a paper mill became dangerously heated, owing to oxidation arising from local high temperature and an air-purging procedure.

Carbon (active)

See Carbon: Turpentine

Diatomaceous earth

Anon., *Ind. Eng. Chem.*, 1950, **42**(7), 77A

A large quantity of discoloured (and peroxidised) turpentine was heated with fuller's earth to decolourise it, and it subsequently exploded. Fuller's earth causes exothermic catalytic decomposition of peroxides and rearrangement of the terpene molecule.

Halogens, or Oxidants, or Tin(IV) chloride

Mellor, 1941, Vol. 2, 11, 90; 1941, Vol. 7, 446; 1943, Vol. 11, 395

Turpentine ignites in contact with fluorine (at —210°C), chlorine, iodine, chromium trioxide, and chromyl chloride, and usually with tin(IV) chloride. Other highly unsaturated hydrocarbons may be expected to react similarly.

Other reactants

Yoshida, 1980, 290

MRH values calculated for 13 combinations with oxidants are given.

Nitric acid: Hydrocarbons (reference 16) MRH 6.03/82, 4430

See Calcium hypochlorite: Turpentine

UNIT PROCESS OR UNIT OPERATION INCIDENTS

1. Shabica, A. C., *Chem. Eng. Progr.*, 1963, **59**(9), 57-66
2. *Organic Chemical Manufacturing Hazards*, Goldfarb, A. S. et al., Zurich, Technomic Publishing, 1981
3. *Control of Industrial Chemical Hazards*, Carson, P. A. et al., Harlow UK, Longmans, (2 Vols) 1989
4. *Hazards of Commercial Chemical Reactions; Hazards of Commercial Chemical Operations*, Austin, G. T., Chs. 4, 5 in *SAFety and Accident Prevention in Chemical Operations*, Fawcett, H. H. and Wood, W. S. (eds), New York, Wiley, 2nd edn., 1982

In a paper on the qualitative evaluation of hazards in organic batch chemical processing operations, the following types of reaction are rated for hazard on a scale of A—E. Reduction (13 methods); oxidation (13 methods); alkylation, C—C (13 methods), C—O (5 methods), C—N (5 methods); condensation (16 methods); amination (3 methods); esterification (9 methods); hydrolysis; substitution; peroxide preparations (2 methods); pyrolysis (2 methods); Schmidt reation; Mannich reaction; halogenation (3 methods); nitration (2 methods). Some 200 common reagents and solvents are also hazard-rated, and general precautions and techniques to avoid batch processing hazards are listed [1]. Three later texts deal with the hazards of specific industrial processes or groups of products [2,3], or with unit processes or operations [4].

Incidents have been grouped for each of the unit process or unit operation headings:

AGITATION INCIDENTS
AMINATION INCIDENTS
CATALYTIC NITRO REDUCTION PROCESSES
DIAZOTISATION
DRYING
EPOXIDATION
GAS EVOLUTION INCIDENTS
GRIGNARD REAGENTS
HALOGENATION INCIDENTS
HYDROGENATION INCIDENTS
IRRADIATION DECOMPOSITION INCIDENTS
MIXING
NEUTRALISATION INCIDENTS

NITRATION INCIDENTS
OXIDATION INCIDENTS
PEROXIDATION INCIDENTS
PLANT CLEANING INCIDENTS
POLYCONDENSATION REACTION INCIDENTS
POLYMERISATION INCIDENTS
REDOX REACTIONS
SULFONATION INCIDENTS

UNSATURATED OILS

See Linseed oil
Carbon: Unsaturated oils, 0297

URANYL MACROCYCLIC PERCHLORATE LIGANDS

Vidali, M. *et al., J. Inorg. Nucl. Chem.*, 1975, **37**, 1715—1719

A series of uranyl complexes of macrocyclic azomethines were used as ligands for transition metal ions, with perchlorate anions. Raman spectra of the uranyl—metal complexes could not be recorded because the samples exploded during attempted measurements.

See other AMMINEMETAL OXOSALTS, IRRADIATION DECOMPOSITION INCIDENTS

VACUUM DISTILLATION RESIDUES

1. Editor's comments, 1995
2. Cardillo, P. *et al., Chem. Abs.*, 1998, **128**, 118814h
3. Cozzani, V. *et al., J. Hazard. Mat.*, 1999, **67**(2), 145

Explosions shortly after the completion of vacuum distillations are common. There are two causes, firstly that the residues are unstable and, heat removal declining with the cessation of agitation and evaporation, there is unaided thermal runaway from the elevated temperature at which such distillations commonly finish. The second is that the still very hot vessel has been repressurised with air, and residues are usually combustible. Cooling of such residues should be checked, if not assisted, and air not admitted to the vessel until it is below 100°C [1]. An account of the investigation of an industrial accident of the first type is available [2]. Investigation after an accident at a solvent recovery plant showed that the vast majority of solvents submitted for recovery contained exothermically unstable residues [3].

Some examples: 4-Chloro-2-methylaniline2-Chloro-4-nitrotoluene: Sodium hydroxide 2-Nitrobenzaldehyde (reference 4) 4-Nitrophenylacetic acid: Acetic anhydride, Pyridine 4-Nitrotoluene (reference 3)

See also COOL FLAMES

VACUUM OVENS

There are potential hazards associated with use of these for drying hectogram scale samples in the laboratory. The vent pipe is usually of small diameter, so the oven pressurises easily should the contents deflagrate, and has no emergency venting system. [The editor has just escaped a door blown open by an ill-washed mononitropyrimidine in his time]. They are commonly installed in the open laboratory, rather than in a fume hood, in possibly false confidence that fumes will go down the vacuum line to the pump-vent. The pump employed is often too feeble to remove substantial quantities of solvent, making an environment often ideal for growth of micro-organisms if a water-wet material is being dried at, the commonly chosen, $<40°C$. Being heavily constructed, thus of high thermal inertia, most designs substantially overshoot the set-temperature on first being turned on. If flammable solvents are being removed, vacuum ovens may be safe while actually under vacuum, but most certainly are not if an incomplete drying is repressurised with air, [which the editor has known to cause fatality on industrial scale].A fan-oven will usually dry large samples faster, has a large vent and will normally be installed within a fume-hood. Only on solvent recovery and flammable limits is it inferior, though less likely to generate electrostatic charges than a repressurised vacuum oven, especially when the latter had condensate in the lines to form a mist.

VACUUM PUMPS

1. Ripper, L. J., *Vak. Praxis*, 1994, **6**(2), 91; *Chem. Abs.*, 1995, **122**, 87800v
2. Oliver, G., *Chemical Engineer*, 1996, (619), s21
3. Grabs, E., *PTB-Mitt.*, 1996, **106**(5), 345

Some reviews on explosion prevention measures for vacuum pumps have been published, including consideration of possible sources of ignition [1]. The second is a discussion of how to prevent and contain explosions in the various cavities of dry vacuum pumps where fuel/oxygen mixes may be present. In view of the ability of oil pumps to generate mists, they may be an even greater danger than dry ones [2]. Another review of vac. pumps pumping potentially explosive mixtures, e.g. in fuel recovery at filling stations, has been written [3].

See Oxygen: Plastic tubes

VANADOCENES

Preparative hazard

Belot, J. A. *et al., Organometallics*, 1996, **15**(23), 5062

A general procedure for producing vanadocenes from reaction of alkali (alkyl)cyclopentadienide and vanadium trichloride in tetrahydofuran produces an extremely pyrophoric sludge as a byproduct contaminating the crude materials.

VAPOUR CLOUD EXPLOSIONS

1. van Wingerden, C. J. M. *et al., Plant/Oper. Progr.*, 1989, **8**(4), 234
2. Johnson, D. M. *et al., Hazards XI*, 67, Symp. Ser. **124**, Rugby (UK), IChE, 1991
3. Abou Arab, *et al., J. Loss Prev. Process Ind.*, 1991, **4**(3), 202
4. Mercx, W. P. M., *Trans. Inst. Chem. Eng.*, 1992, **70**(B4), 197
5. Anon., *Loss Prev. Bull.*, 1991, **099**
6. Davenport, J. A. *et al., Process Safety Progr.*, 1993, **12**(1), 12
7. Mancini, R. A., *Plant/Oper. Progr.*, 1992, **11**(1), 27; Bull, D. C., *ibid.*, 33

8. Mercx, W. P. M. *et al., Process Safety Progr.*, 1993, **12**(4), 222
9. Mercx, W. P. M. *et al., Process Safety Progr.*, 1995, **14**(2), 121
10. Bjerketvedt, D. *et al., J. Hazard Mat.*, 1997, **52**(1), 1
11. Tang, M. J. *et al., Process Safety Progr.*, 1999, **18**(4), 235.
12. Yang, L. *et al., Process Safety Progr.*, 2000, **19**(2), 103
13. Krasnov, V. M. *et al., J. Atmos. & Solar-Terrest. Phys.*, 2003, **65**(11-13), 1205
14. Venart, J. E. S., *process Safety & Envir. Protect.*, 2004, **82**(B2), 105

This term (or, confusingly, Vapour Explosion) is used for releases of superheated flammable liquids, or gases, followed by ignition after a delay, which may be of some minutes. Overpressures are slight and deflagration slow in open, unobstructed spaces. Obstruction and partial confinement accelerate the flame front and produce blasts such as in the 1974 Flixborough cyclohexane release; a predictive model is described and demonstrated on Flixborough, understanding is not yet complete [1]. There may be substantial delay between ignition and significant overpressure. Experiments and their results with large-scale natural gas release are described [2]. Smaller scale experiment is described [3]. A comparison of large scale experiments with small (even these of several m^3) is given; high energy fuels, especially ethene, show transition to detonation in obstructed spaces [4].The most damaging industrial explosions of the last few decades have been of this nature [5,6]. Detonation does not usually seem to have been involved in such accidents, however studies relating to unconfined detonation initiation in hydrocarbon / air mixes have been made [12]. For reviews of both the theory and experiment: [7]. The development of methods to predict the blast risks is described [8]. Techniques for experimental vapour cloud explosion studies are evaluated [9]. A handbook on (natural) gas explosion safety has been published [10]. Improved calculations for blast overpressure are reported [11]. A TNT equivalence of 3 hectotonnes for Flixborough has been calculated from ionospheric disturbances, which is attributed to only 15 tonnes of cyclohexane [13,14], less than comparison of hydrocarbon combustion and TNT detonation enthalpies would suggest.

See also BLEVE, DEFLAGRATION TO DETONATION, GEOMETRY OF VESSELS AND PIPEWORK, MISTS

VAPOUR EXPLOSIONS

1. Fröhlich, G., *Chem. Ing. Tech.*, 1978, **50**, 861—866
2. Ogiso, C. *et al., Chem. Abs.*, 1985, **102**, 190161
3. Iida, Y. *et al., JSME Int. J.*, 1987, **30**, 1972—1981
4. Fletcher, D. F. *et al., J. Loss Prev.*, 1994, **7**(6), 457
5. Theofanous, T. G. *et al, Phys. Fluids*, 1994, **6**(11), 3513
6. Matsumura, K. *et al., J. Nucl. Sci. Technol.*, 1999, **36**(9), 767
7. Matsumura, K. *et al., Chem. Abs.*, 1999, **130**, 8244f
8. Babaitsev, I. V. *et al., Chem. Abs.*, 2001, **134**, 369761g

A vapour explosion can occur on contact between 2 liquids of differing temperatures if the temperature of the hotter liquid is above the b.p. of the cooler, and the explosion is due to extremely rapid vapour generation (phase transition) of the cooler liquid. Vapour generation must be preceeded by very good heat transfer by a fragmentation

process leading to enormous heat transfer coefficients. Experimental results are discussed for water as the cooler liquid and melts of glass, aluminium, copper, iron, gallium or lead as the hotter liquid. The probability of steam explosions depends on the materials of the melt, the temperatures of the 2 liquids (not only the temperature difference), the reacting masses, the shape of the container and external triggering (by impact, etc.) [1]. An experimental study of vapour explosions of water in contact with sodium carbonate—sodium chloride hot melts is reported [2]. The mechanism of vapour explosions caused by drops of molten lithium nitrate falling into ethanol has been studied by high-speed photography and pressure trace measurements [3]. More recent work in the area is reviewed, with a description of the processes involved. It is suggested that the Krakatoa eruption was the largest incident on record [4]. Interaction of molten aluminium and water is studied, in particular the conditions in which vapour explosion can initiate chemical reaction [5]. A study of vapour explosions from pouring molten tin into water has been published. Dependence upon the dimensions of the water pool, as well as temperatures, was shown [6]. This seems to be modelling for nuclear reactor melt-down hazards [7]. A technique for calculating the TNT equivalence of water mixing with molten iron has been developed (0.5 in the example quoted) [8].
See LIQUEFIED GASES, MOLTEN METAL EXPLOSIONS, SMELT, SUPERHEATED LIQUIDS

VEGETABLE OILS

Catalysts, Hydrogen
See Hydrogen: Catalysts, Vegetable oils

VENT LINES

Chemistry does not limit itself to spaces called reactors. Considerable quantities of dust, mist, and vapours may be transferred to vent lines and fumehood ducts, possibly accumulating and reacting there for years. In consequence fires and explosions can start, or blockages form. Vent lines would be better for occasional scrubbing down.
See Perchloric acid: Fume cupboards
See Silver nitrate: Sodium dithionite

VINYLMERCURY HYDRIDES

Guillemin, J-C. *et al., Inorg. Chem.*, 1996, **35**(22), 6586
These compounds, alk-1-enylmercuranes as they may be known to pedant and pedagogue, are very unstable at room temperature even in solution, decomposing to mercury, hydrogen and the corresponding butadiene in a matter of minutes. Pressurisation of sealed containers would result.

VINYLSILOXANES

Schilling, C. L., *et al., Chem. Eng. News*, 1994, **72**(37), 2
Vinyl siloxanes are prone to uncontrolled exotherm and explosion without other than thermal assistance. There is extremely rapid pressure generation in closed containers from about 200°C.
See SILANES

VINYL SULFOXIDES $C=C.SO_2—$

Nikonov, V. A. *et al., Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, *38*(7,1), 1374; *Chem. Abs*. 1990, **112**, 29847

Complexes of butyl vinyl sulfoxide and iron, chromium and cobalt (III) nitrates were found to be unstable, the ferric salt (the least stable) exploding even as a 40 mol% solution in benzene. It is considered that other vinyl sulfoxide ligands will behave similarly.

See METAL NITRATES

VIOLENT POLYMERISATION

1. Harmon, M. *et al., A Review of Violent Monomer Polymerisation*, Rept. AD-017443, Richmond (Va.), USNTIS, 1974
2. Bond, J., *Loss Prev. Bull.*, 1985 (065), 21—28
3. Frurip, D. J. *et al., Process Safety Progr.*, 1995, **14**(2), 79
4. Ogiso, C. *et al., Chem. Abs.*, 1986, **105**, 29100
5. Encyclop. Polym. Sci. Eng., Mark, H. F. *et al.* (eds), Vol. 14, 805—827, New York, Wiley, 1988
6. Thomas, I. F. in *Integrated Risk Management* (Eds: Melchers & Stewart), 177, Rotterdam, Balkema,1995

Radical polymerisations, in particular, are liable to run out of control. There are three reasons for this; firstly monomers may contain traces of inhibitors, in which case the rate of polymerisation will rise when these are exhausted, secondly the physics of polymer solution cause the termination rate of radical chains to decline as the reaction proceeds, meaning acceleration and increased heat evolution exactly when increasing viscosity makes it difficult to remove (the Norrish—Tromsdorff effect). The third possibility is ‘popcorn polymerisation’ (so called from the appearance of the product) which is a spontaneous event, usually during storage, in which polymer gel particles are thought to be osmotically swollen by penetrating monomer to the degree of rupturing bonds: more radicals and, effectively, a branched chain process.

Literature related to the possibility of violent polymerisation of the 10 monomers most significant industrially has been classified and reviewed, and 209 annotated references are given. The compounds covered are acrylic acid, acrylonitrile, 1,3-butadiene, ethylene, ethylene oxide, methyl acrylate, methyl methacrylate, propiolactone, styrene, vinyl acetate, vinyl chloride and vinylidene chloride. Almost all have been involved in explosive polymerisation incidents. For each compound, data and selected references on physical properties, reactivity, inhibition and handling procedures are given [1]. Mechanisms of initiation, inhibition, and de-inhibition of polymerisation are reviewed briefly, with 8 case histories of incidents involving violent polymerisation of 6 common monomers [2]. A procedure is given for assessing monomers for risk of runaway polymerisation [3]. Conditions for runaway reactions in suspension polymerisation when stirring is stopped were determined experimentally. A vapour explosion was observed in a closed system under runaway conditions [4]. A 22-page section devoted to safety aspects of the production and uses of polymeric materials covers a wide range of relevant topics in polymerisation and processing plant management, including a comprehensive reference list [5].

Acrylic monomers, in particular, are inclined to polymerisation in the absence of oxygen which serves as a chain-breaker in their radical polymerisation. Most such monomers are also flammable and may therefore be directed to be stored under a nitrogen blanket. If nitrogen purging is complete, the risk of fire within vessels may be zero, but the risk of explosive polymerisation, tank-rupture and external fire is increased. Some suspect that accidents of this type have occurred already [6].

Detailed examples may be found in the entries:

† Acrylonitrile, : Initiators, 1104
† 1,3-Butadiene, 1476
† 1,2-Butadiene, 1475
† 1,1-Dichloroethylene, 0691
† Ethylene, 0777
† Ethylene oxide, : Ammonia, 0825
† Methyl acrylate, 1526
See ACRYLIC MONOMERS
See also POLYMERISATION INCIDENTS

WASTE DISPOSAL

See DISPOSAL

WASTE SOLVENT BOTTLE

Time was when laboratory waste solvents, and reagents, went to drain, sometimes causing sewer explosions if the solvents were flammable and water immiscible. Then came environmentalism. In the 1990s, exploding waste solvent bottles are probably the most common cause of serious laboratory accidents in the academic sector. The usual cause seems to be putting nitric acid into this bottle. Nitric acid is not to be trusted with any organic solvent, even chlorinated ones. Considering how much nitric acid the environment makes and how little man in laboratory handles, a rational being might still hold the drain, with plenty of water, the safest place for it. The same cannot be said of chromic acid and dichromates, which are also sometimes mixed with waste solvent, to explosive effect. Less violent, but bad enough, are inadvertent Friedel Crafts reactions caused by mixing halides and aromatic wastes, Formerly, mixing acetone and chloroform caused problems, but the environmentalists have since proscribed chloroform and laboratories instituted separate bottles for chlorinated solvents. Promiscuous mixing of, sometimes unknown, liquids is fraught with hazard!

See Chloroform: Acetone, Alkali
See Nitric acid
See Sulfuric acid: Waste solvents
See also ENVIRONMENTALISM

WATER-REACTIVE COMPOUNDS

A large number of individual compounds react exothermally and violently with water, particularly with restricted amounts of the latter. Many such compounds come within the groups:

ACID ANHYDRIDES
ACYL HALIDES
ALKALI METALS
ALKYLALUMINIUM DERIVATIVES
ALKYLNON-METAL HALIDES
COMPLEX HYDRIDES
METAL HALIDES
METAL HYDRIDES
METAL OXIDES
NON-METAL HALIDES (AND THEIR OXIDES)
NON-METAL OXIDES

WAX FIRE

Carbon tetrachloride

1. Gilmont, R., *Chem. Eng. News*, 1947, **25**, 2853
2. Author's comment, 1989

Use of carbon tetrachloride to extinguish a wax fire caused an explosion. This was attributed to a violent reaction between unsaturated wax components and carbon tetrachloride initiated by radicals from decomposing peroxides [1]. Perhaps a more likely explanation could be that contact of the cold low-boiling liquid with the hot molten wax led to the physical effect of a vapour explosion, rather than the chemical explosion postulated [2].

See Dibenzoyl peroxide: Carbon tetrachloride

WOOD PULP

Eidsan, G. *et al., Biotechnol. Lett.*, 1979, **1**, 31—34

Semi-chemical pulp contaminated with micro-organisms and incubated at 60°C produces a hydrogen-containing gas. A gas-phase explosion in a pulp storage tower was attributed to static ignition of this gas admixed with air.

See other STATIC INITIATION INCIDENTS

WOOL

Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345—351

The self-heating and ignition of baled or loose wool in bulk storage is discussed and analysed, and steady state thermal explosion theory is applied to the prediction of critical masses and induction periods for storage and transportation situations in relation to ambient temperature. Results obtained were consistent with current safety practices.

WORKERS AT THE NEXT BENCH

Are almost as dangerous as are you, dear reader. Make sure you know what he is doing and expect her to return the compliment.

‘XANTHATES’ ROC(S)S$^-$

1. Sorbe, 1968, 74
2. Anon., Private communication, 1990
3. Kirk-Othmer, 1984, 3rd Edn., Vol. 24, 646

Salts of *O*-alkyldithiocarbonates (‘xanthates’) are hazardous as dusts, forming explosive suspensions in air. The lower-alkyl salts are claimed to be explosive in the solid state when dry [1]. Explosions reported when drying hydrated xanthate salts are probably the consequence of release of carbon disulphide to form an inflammable atmosphere of very low autoignition temperature in the oven [2]. Xanthate esters are thermally unstable by a variety of eliminations and rearrangements, all distinctly exothermic and many evolving extremely flammable gases and vapours. Free xanthic acids, which may be isolated on acidification, decompose autocatalytically and perhaps explosively [3].

See Potassium *O*-ethyl dithiocarbonate
See also CARBON DISULFIDE

Diazonium salts
See DIAZONIUM SULFIDES AND DERIVATIVES (reference 8)

XENON COMPOUNDS Xe—F, Xe—O

1. Jha, N. K., *RIC Rev.*, 1971, **4**, 16765168
2. Kirk-Othmer, 3rd Edn., 1980, Vol. 12, 293; 4th Edn, 1995, Vol 13, 9

For convenience, the even rarer and less stable krypton compounds are also covered in this entry. All xenon compounds are very strong oxidants and many are also explosively unstable. For a now obsolete review, see [1]. A compact review of noble gas chemistry is found in [2]. A series of alkali xenates, $MHOXeO_3.1.5H_2O$ are unstable explosive solids. The equivalent fluoroxenates $MFXeO_3$ are far more stable. Individually indexed compounds are:

Caesium bromoxenate, 0237
Caesium chloroxenate, 3964
Caesium hydrogen xenate, 4253
* Krypton difluoride, 4307
Potassium hexaoxoxenonate—xenon trioxide, 4669
Tetrafluoroammonium hexafluoroxenate, 4380
Xenon difluoride, 4326
Xenon difluoride dioxide, 4316
Xenon difluoride oxide, 4313
Xenon hexafluoride, 4371
Xenon tetrafluoride, 4347
Xenon tetrafluoride oxide, 4340
Xenon tetraoxide, 4857

Xenon trioxide, 4851
Xenon(II) fluoride methanesulfonate, 0442
Xenon(II) fluoride perchlorate, 3971
Xenon(II) fluoride trifluoroacetate, 0630
Xenon(II) fluoride trifluoromethanesulfonate, 0355
Xenon(II) pentafluoroorthoselenate, 4376
Xenon(II) pentafluoroorthotellurate, 4377
Xenon(II) perchlorate, 4104
Xenon(IV) hydroxide, 4528
See other NON-METAL HALIDES, NON-METAL OXIDES

YEAST

1. Anon., *The Daily Telegraph* (London), Jan. 30th 1996, 6
2. Editor's comments

A package of brewers' yeast exploded, slightly injuring three postal workers [1]. Fermentations in sealed containers can easily generate sufficient pressure of carbon dioxide to rupture the container. The problem is well known to home ginger beer makers and Champagne houses; now that yeast is sometimes used as a reducing agent it is appearing in the chemical world [2].
See SUGARS

ZINC BACITRACIN

Piotrowski, T., *Chem. Abs.*, 1984, **101**, 60040
In a study of explosive potential of 20 pharmaceutical products, zinc bacitracin was identified as unusual, in that though not normally explosive, when it does explode it produces relatively high pressures.
See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Appendix 1

Source Title Abbreviations used in Handbook References

The abbreviations used in the references for titles of journals and periodicals are those used in BP publications practice and conform closely to the recommendations of the *Chemical Abstracts* system. Abbreviations which have been used to indicate textbook and reference book sources of information are set out below with the full titles and publication details.

ABCM Quart. Safety Summ.,	*Quarterly Safety Summaries*, London, Association of British Chemical Manufacturers, 1930–1964
ACS 54, 1966	*Advanced Propellant Chemistry*, ACS 54, Washington, American Chemical Society, 1966
ACS 88, 1969	*Propellants Manufacture, Hazards and Testing*, ACS 88, Washington, American Chemical Society, 1969
Albright, Hanson, 1976	*Industrial and Laboratory Nitrations*, ACS Symposium Series 22, Albright, L. F., Hanson, C., (Eds.), Washington, American Chemical Society, 1976
Alkali Metals, 1957	*Alkali Metals*, ACS 19, Washington, American Chemical Society, 1957
ASHRAE. J.	*American Society of Heating, Refrigeration and Air-conditioning Engineers Journal*, New York.
Augustine, 1968	*Reduction, Techniques and Applications in Organic Chemistry*, Augustine, R. L., London, Edward Arnold, 1968

Augustine, 1969, 1971	*Oxidation, Techniques and Applications in Organic Synthesis*, Augustine, R. L., (Ed.), New York, Marcel Dekker, Vol. 1, 1968, Vol. 2 (with Trecker, D. J.), 1971
Bahme, 1972	*Fire Officer's Guide to Dangerous Chemicals*, FSP-36, Bahme, C. W., Boston, National Fire Protection Association, 1972
Bailar, 1973	*Comprehensive Inorganic Chemistry*, Bailar, J. C., Emeléus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., (Eds.), Oxford, Pergamon, 5 vols., 1973
BCISC Quart. Safety Summ.,	*Quarterly Safety Summaries*, London, British Chemical Industries Safety Council, 1965–1973
Barton & Ollis, 1979	*Comprehensive Organic Chemistry*, Barton, D. H. R., Ollis, W. D., (Eds), Oxford, Pergamon, 1979.
Biasutti, 1981	*History of Accidents in the Explosives Industry*, Biasutti, G. S. (Author and publisher), Vevey, 1981
Bond, 1991	*Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991
Braker, 1981	*Matheson Gas Data Book*, Braker, W., Mossman, A. L., Lyndhurst (NJ), Matheson Div. Searle, 6th edn. 1981
Brandsma, 1971	*Preparative Acetylenic Chemistry*, Brandsma, L., Barking, Elsevier, 1971
Brauer, 1961, 1965	*Handbook of Preparative Inorganic Chemistry*, Brauer, G., (Translation Ed. Riley, R. F.), London, Academic Press, 2nd edn. Vol. 1, 1963; Vol. 2, 1965
Bretherick, 1986	*Hazards in the Chemical Laboratory*, Bretherick, L. (Ed.), London, Royal Society of Chemistry, 4th edn., 1986
Castrantas, 1965	*Fire and Explosion Hazards of Peroxy Compounds*, Special Publication No. 394, Castrantas, H. M., Banerjee, D. K., Noller, D. C., Philadelphia, ASTM, 1965
Castrantas, 1970	*Laboratory Handling and Storage of Peroxy Compounds*, Special Publication No. 491, Castrantas, H. M., Banerjee, D. K., Philadelphia, ASTM, 1970

CHAS Notes	*Chemical Health and Safety Notes*, ACS Division of Chemical Health and Safety, Washington, 1982 to date (4 issues/yr)
Chemiarbeit	*Chemiearbeit, Schutzen und Helfen*, Dusseldorf, Berufsgenossenschaft der Chemische Industrie, 1949–1962 (supplement to Chemische Industrie)
Chem. Hazards Ind.	*Chemical Hazards in Industry*, Royal Society of Chemistry Information Group, Cambridge, 1984 to date (monthly abstracts)
CISHC Chem. Safety Summ.,	*Chemical Safety Summaries*, London, Chemical Industry Safety and Health Council of the Chemical Industries Association, 1974 to 1986 (terminated)
CHETAH 1990	*The ASTM Chemical Thermodynamic and Energy Release Evaluation Programme*, Version 4.4, 2nd Edn (ASTM Data Series Publication 51A), Davies C. A. *et al.*, Philadelphia, ASTM, Appendix V. Upgrades continue to be issued (1998)
Cloyd, 1965	*Handling Hazardous Materials*, Technical Survey No. SP-5032, Cloyd, D. R., Murphy, W. J., Washington, NASA, 1965
Coates, 1960	*Organometallic Compounds*, Coates, G. E., London, Methuen, 1960
Coates, 1967, 1968	*Organometallic Compounds*, Coates, G. E., Green, M. L. H., Wade, K., London, Methuen, Vol. 1, 1967, Vol. 2, 1968
Compendium 1985, 1987	*Compendium of Safety Data Sheets, for Research and Industrial Chemicals*, Keith, L. H., Walters, D. B., Deerfield Beach/Weinheim, VCH, vols. 1–3 of 867 sheets 1985, vols 4–6 of 723 sheets, 1987
Dangerous Loads, 1972	*Dangerous Loads*, Leicester, Institution of Fire Engineers, 1972
Dangerous Substances, 1972	*Dangerous Substances: Guidance on Fires and Spillages* (Section 1, 'Inflammable liquids'), London, HMSO, 1972
Davies, 1961	*Organic Peroxides*, Davies, A. G., London, Butterworths, 1961
Davis, 1943	*Chemistry of Powder and Explosives*, Davis, T. L., New York, Wiley, 1943

DOC 5, 1982	*Dictionary of Organic Compounds*, Buckingham, J., (Ed.), London, Chapman & Hall, 5th edn. in 5 vols. + indices, 1982, annual supplementary vols. to date
Dunlop, 1953	*The Furans*, ACS 119, Dunlop, A. P., Peters, F. N., New York, Reinhold, 1953
Ellern, 1968	*Military and Civilian Pyrotechnics*, Ellern, H., New York, Chemical Publishing Co., 1968
Emeléus, 1960	*Modern Aspects of Inorganic Chemistry*, Emeléus, H. J., Anderson, J. S., London, Rutledge and Kegan Paul, 1960
Ephraim, 1939	*Inorganic Chemistry*, Ephraim, F., (3rd Engl. edn., Thorne, P. C. L., Ward, A. M.), London, Gurney & Jackson, 1939
Federoff, 1960	*Encyclopaedia of Explosives and Related Compounds*, Federoff, B. T. (Ed.), Dover (NJ), Piccatinny Arsenal, Vol. 1, 1960; Vol. 10, 1984 (from USNTIS)
Fieser, 1967–1986	*Reagents for Organic Synthesis*, Fieser, L. F. and Fieser, M., New York, Wiley, Vol. 1, 1967, The series continues after the death of the originator.
Freifelder, 1971	*Practical Catalytic Hydrogenation*, Freifelder, M., New York, Wiley-Interscience, 1971
Gallais, 1957	*Chimie Minérale Théoretique et Expérimental (Chimie Électronique)*, Gallais, F., Paris, Masson, 1957
Gaylord, 1956	*Reductions with Complex Metal Hydrides*, Gaylord, N. G., New York, Interscience, 1956
Gibson, 1969	*Handbook of Selected Properties of Air-and Water-Reactive Materials*, Gibson, H., Crane (In.), US Naval Ammunition Depot, 1969
Goehring, 1957	*Ergebnisse und Probleme der Chemie der Schwefelstickstoff-verbindung, Scientia Chemica*, Vol. 9, Goehring, M., Berlin, Akademie Verlag, 1957
Grignard, 1935–54	*Traité de Chimie Organique*, Grignard, V. and various volume Eds., Paris, Masson, Vol. 1, 1935, Vol. 23, 1954

Guide for Safety, 1972	*Guide for Safety in the Chemical Laboratory*, MCA, New York, Van Nostrand Reinhold, 2nd edn., 1972
Harmon, 1974	*A Review of Violent Monomer Polymerisation*, Harmon, M., King, J., Rept. AD-017443, Springfield (Va.), NTIS, 1974
Haz. Chem. Data, 1975	*Hazardous Chemical Data*, NFPA 49, Boston, National Fire Protection Association, 1975
HCS 1980	*Handling Chemicals Safely*, Dutch Assoc. of Safety Experts, Dutch Chemical Industry Assoc., Dutch Safety Inst., 1980 (Engl. transl. of 2nd Dutch edn.)
Houben-Weyl, 1953 to date	*Methoden der Organischen Chemie*, Müller, E. (Ed.), Stuttgart, Georg Thieme, 4th edn., published unsequentially from 1953.
Inorg. Synth., 1939–86	*Inorganic Syntheses*, various Eds., Maidenhead, McGraw-Hill, Vol. 1, 1939, Vol. 24, 1986
Jahresber. 1960 to date	*Jahresberichte*, Berufsgenossenschaft der Chemischen Industrie, Heidelberg, annually since 1960
JANAF, 1971	*JANAF Thermochemical Tables*, Stull, D. R., Prophet, H., National Bureau of Standards, 2nd edn., 1971
Karrer, 1950	*Organic Chemistry*, Karrer, P., London, Elsevier, 1950
Janz, 1976	*Eutectic Data, Table 2 (Safety Hazards, etc.)* Janz, G. J., Allen, C. B., Molten Salts Data Center, ERDA Rept. TID 27163-21, 1976; subsequently publ. in J. Haz. Mat., 1980–81, **4** (1), 145–176
Kharasch and Reinmuth, 1954	*Grignard Reactions of Non-Metallic Substances*, Kharasch, M. S. and Reinmuth, O., London, Constable, 1954
King, 1990	*Safety in the Process Industries*, King, R., London, Butterworth-Heinemann, 1990
Kirk-Othmer, 1963–71	*Encyclopaedia of Chemical Technology*, (3rd edn., 1978–83) Kirk, R. E., Othmer, D. F., London, Wiley-Interscience, Vol. 1, 1963, Vol. 22, 1970, Suppl. Vol. 1971. (4th edn., from 1991) 1993;

Kirshenbaum, 1956	*Final Report on Fundamental Studies of New Explosive Reactions*, Kirshenbaum, A. D., Philadelphia, Research Institute of Temple University, 1956
Kit and Evered, 1960	*Rocket Propellant Handbook*, Kit, B., Evered, D. S., London, MacMillan, 1960
Lab. Hazards Bull.	*Laboratory Hazards Bulletin*, Royal Society of Chemistry Information Group, Cambridge, 1981 to date (monthly abstracts)
Lawless, 1968	*High Energy Oxidisers*, Lawless, E. W. and Smith, I. C., New York, Marcel Dekker, 1968
Leleu, Cahiers, 1972–80	*Les Réactions Chimique Dangereuse*, Leleu, J., published serially in *Cahiers de Notes Documentaires*, from 1972 **(68)**, 319 to 1980, **(100)**, 426
Loss Prev. Bull., 1974 to date	*Loss Prevention Bulletin*, Rugby, Institution of Chemical Engineers, 6 issues annually since 1974
Mackay, 1966	*Hydrogen Compounds of the Metallic Elements*, Mackay, K. M., London, Spon, 1966
Major Loss Prevention, 1971	*Major Loss Prevention in the Process Industries, Symposium Series* No. 34, London, Institution of Chemical Engineers, 1971
Martin, 1971	*Dimethylsulfoxid*, Martin, D., Hauthal, H. G., Berlin, Akademie Verlag, 1971
Matheson Guide, 1982	*Guide to Safe Handling of Compressed Gases*, Matheson Div. Searle Medical Products, Lyndhurst (NJ), 1982
MCA Case Histories, 1950–78	*Case Histories of Accidents in the Chemical Industry*, Washington, MCA, (published monthly, republished as 4 ndexed collected volumes 1953–75, discontinued 1978)
(MCA SD-Series) 1947–76	*Safety Data Sheets*, MCA, Washington. The whole series of 101 sheets was withdrawn in 1980, but remains a useful source of collected information on basic industrial chemicals.
Meidl, 1972	*Hazardous Materials Handbook*, Meidl, J. H., Beverley Hills, Glencoe Press, 1972

Mellor, 1947–71	*Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Mellor, J. W., London, Longmans Green, Vol. 1, repr. 1941, Vol. 16, publ. 1937; and isolated Supplementary vols. up to Vol. 8 Suppl. 3, 1971
Mellor MIC, 1961	*Mellor's Modern Inorganic Chemistry*, Parkes, G. D. (Revision Ed.), London, Longmans Green, 1961
Merck, 1976, 1983, 1989, 1996	*The Merck Index*, Chapman and Hall, London., 9th edn. 1976, 10th edn. 1983, 11th edn. 1989, 12th edn. 1996
Merrifield, 1988	*Fire and Explosion Hazards associated with Storage and Handling of Hydrogen Peroxide*, Merrifield, R., Specialist Inspectors Report No. 19, Bootle, HSE. 1988
Meyer, 1977	*Chemistry of Hazardous Materials*, Meyer, E., Englewood Cliffs (NJ), Prentice-Hall, 1977
Miller, 1965–66	*Acetylene, its Properties, Manufacture and Uses*, Miller, S. A., London, Academic Press, Vol. 1, 1965, Vol. 2, 1966
Moissan, 1900	*Le Fluor et ses Composés*, Moissan, H., Paris, Steinheil, 1900
NFPA 491M, 1975	*Manual of Hazardous Chemical Reactions*, NFPA 491M, Quincy (MA), National Fire Potection Association, 5th edn., 1975 (larger format of same text, 1985)
Nolan, 1983	*Case Histories of Runaway Reactions*, Nolan, P. F., London, Polytechnic of the South Bank, 1983. A summary of the conclusions on the causes was published in *J. Haz. Materials*, 1987, **14**, 233–239
Org. Synth., 1941 to date	*Organic Syntheses*, various Eds., New York, Wiley, Collective Vol. 1, 1944; Coll. Vol. 2, 1944; Coll. Vol. 3, 1955; Coll. Vol. 4, 1962; Coll. Vol. 5, 1973; Coll. Vol. 6, 1987; Coll. Vol. 7, 1990; Coll. Vol. 8, 1993; annual volumes (from 70) thereafter.
Partington, 1967	*General and Inorganic Chemistry*, Partington, J. R., London, MacMillan, 4th edn., 1967

Pascal, 1956–70	*Nouveau Traité de Chimie Minérale*, Pascal, P. (Ed.), Paris, Masson, Vol. 1, 1956; Vol. 20.3, 1964; Vol. 15.5, 1970
Pieters, 1957	*Safety in the Chemical Laboratory*, Pieters, H. A. J., Creyghton, J. W., London, Academic Press, 2nd edn., 1957
Plant/Oper. Progress	*Plant Operations Progress* continues as *Process Safety Progress* 1993-
Pot. Incid. Rept.	*ASESB Potential Incident Report*, Washington, Armed Services Explosives Safety Board
Proc. nth Combust. Symp.	*Proceedings of Combustion Symposia*, various Eds. and Publishers, dated year following the event. 1st Symposium 1928; 19th Symposium, 1982
Renfrew, 1981	*Safety in the Chemical Laboratory*, Collected reprinted articles from *J. Chem. Educ.*, Renfrew, M. M. (Ed.), Vol. IV, 1981
Rodd, 1951–62	*The Chemistry of Carbon Compounds*, Rodd, E. H. (Ed.), London, Elsevier, Vol. 1A, 1951, Vol. 5, 1962; 2nd edn. began in 1979
RSC Data Sheets, 1982 to date	*Laboratory Hazard Data Sheet Series*, Cambridge, Royal Society of Chemistry, No. 1, 1982; No. 89, 1989, issued monthly, ceased 1993
RSC Safety Data Sheets, 1989	*Chemical Safety Data Sheets*, Cambridge, Royal Society of Chemistry, 1989 Generally similar to the monthly Laboratory Hazards Safety Data Sheet series, but the information is presented under headings reflecting legislative requirements. Volume 1 deals with some 100 largely organic liquid solvents and reagents, while Volume 2 covers main group metals and their compounds, 122 items in all. Vol. 3; Corrosives and Irritants, 1990. Vol 4; Toxic Chemicals, Pt. I 1990, Pt. II 1991. Vol 5, Flammables, 1989. There is considerable overlap among the volumes
Runaway Reactions, 1981	*Runaway Reactions, Unstable Products and Combustible Powders*, Symposium-Series No. 68 (Chester 1981), Rugby, Institution of Chemical Engineers, 1981

Rüst, 1948	*Unfälle beim Chemischen Arbeiten*, Rüst, E., Ebert, A., Zurich, Rascher Verlag, 2nd edn., 1948
Rutledge, 1968	*Acetylenic Compounds*, Rutledge, T. F., New York, Reinhold, 1968
Schmidt, 1967	*Handling and Use of Fluorine and Flourine-Oxygen Mixtures in Rocket Systems*, SP-3037, Schmidt, H. W., Harper, J. T., Washington, NASA, 1967
Schumacher, 1960	*Perchlorates, their Properties, Manufacture and uses*, ACS 146, Schumacher, J. C., New York, Reinhold, 1960
Schumb, 1955	*Hydrogen Peroxide*, ACS 128, Schumb, W. C., Satterfield, C. N., Wentworth, R. L., New York, Reinhold, 1955
Shriver, 1986	*Manipulation of Air-Sensitive Compounds*, Shriver, D. F. and Drozdzon, M. A. (Eds.), New York, Wiley, 2nd edn., 1986
Sichere Chemiearb.	*Sichere Chemiarbeit*, Heidelberg, Berufsgenossenschaft der Chemischen Industrie, 1963 to date
Sidgwick, 1950	*The Chemical Elements and their Compounds*, Sidgwick, N. V., Oxford, Oxford University Press, 1950
Sittig, 1981	*Handbook of Toxic and Hazardous Chemicals*, Sittig, M., Park Ridge (NJ), Noyes Data Corp., 2nd ed., 1985
Smith, 1965–6	*Open-Chain Nitrogen Compounds*, Smith, P. A. S., New York, Benjamin, Vol. 1, 1965; Vol. 2, 1966
Sorbe, 1968	*Giftige und Explosive Substanzen*, Sorbe, G., Frankfurt, Umschau Verlag, 1968
Steere, 1971	*Handbook of Laboratory Safety*, Steere, N. V. (Ed.), Cleveland, Chemical Rubber Publishing Co., 2nd edn., 1971. 3rd edn., Furr, A. K. (Ed.), 1989
Steere, 1967, ’71, ’74	*Safety in the Chemical Laboratory*, N. V. Steere (Ed.), Collected reprinted articles from *J. Chem. Educ.*, Vol. I, 1967; Vol. II, 1971; Vol. III, 1974

Stull, 1977	*Fundamentals of Fire and Explosion*, AIChE Monograph Series No. 10, Stull, D. R., New York, American Institute of Chemical Engineers, 1977
Swern, 1970–52	*Organic Peroxides*, Swern, D. (Ed.), London, Wiley-Interscience, Vol. 1, 1970; Vol. 2, 1971; Vol. 3, 1972
Ullmann, 1998	*Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, 6th edn. 1998 (CD update 1999)
Urbanski, 1964–84	*Chemistry and Technology of Explosives*, Urbanski, T., London, MacMillan, Vol. 1, 1964; Vol. 2, 1965; Vol. 3, 1967; Oxford, Pergamon, Vol. 4, 1984
Van Wazer, 1958–61	*Phosphorus and its Compounds*, Van Wazer, J. R., New York, Interscience, Vol. 1, 1958; Vol. 2, 1961
Vervalin, 1973	*Fire Protection Manual for Hydrocarbon Processing Plants*, Vervalin, C. H. (Ed.), Houston, Gulf Publishing Co., 2nd edn., 1973
Vogel, 1957	*A Textbook of Practical Organic Chemistry*, Vogel, A. I., London, Longmans Green, 3rd edn., 1957
von Schwartz, 1918	*Fire and Explosion Risks*, von Schwartz, E., London, Griffin, 1918
Weast, 1988	*Handbook of Chemistry and Physics*, Weast, R. C. (Ed.), Boca Raton (Fa.), CRC Press, 1988; continued under the editorship of Lide, D. R.
Whitmore, 1921	*Organic Compounds of Mercury*, Whitmore, F. C., New York, Chemical Catalog Co. Inc., 1921
Yoshida, 1980	*Handbook of Hazardous Reactions with Chemicals*, Yoshida, T., Tokyo, Tokyo Fire Department, 1980 (copy in British Library, Boston Spa)
Zabetakis, 1965	*Flammability Characteristics of Combustible Gases and Vapours*, Zabetakis, M. G., Washington, US Bureau of Mines, 1965

Appendix 2

Glossary of Abbreviations and Technical Terms

ABS	A plastic which is a copolymer of acrylonitrile, butadiene and styrene
Aerobic	In presence of air
AIT	Autoignition temperature
Alloy	Mixture of 2 or more metals
Amalgam	Alloy of a metal with mercury
Ambient	Usual or surrounding
Anaerobic	In absence of air
Analogue	Compound of the same structural type
AO	Active oxygen content of peroxides
Aprotic	Without labile hydrogen atom(s)
Aqua regia	Mixture of nitric and hydrochloric acids
ARC	Accelerating rate calorimetry
ASTM	American Society for Testing and Materials
Autocatalytic	A reaction catalysed by its own products or intermediates, thus Self Accelerating
Autoxidation	Slow reaction with air
BAM	Bundes Anstalt für Materialsprüfung (similar to ASTM)
Basic	Fundamental, or, alkaline (acting as a base)
BLEVE	Boiling liquid expanding vapour explosion
Blowing agent	Material producing much gas on decomposition
b.p.	Boiling point
BSC	Bench scale calorimeter
Carbonaceous	Containing elemental carbon (as opposed to organic, containing combined carbon)
CHETAH	A computer program to predict energy release hazards
CIT	Critical ignition temperature
Class	Collection of related chemical groups or topics
COI	Critical oxygen index
conc.	concentrated
Congener	Compound with related but not identical structure
COT	Cyclooctatetraene

Cp	Cyclopentadienyl
Critical diameter	Minimum diameter of an explosive charge capable of maintaining detonation
Cryogenic	At a very low (freezing) temperature
CVD	Chemical vapour deposition
Deflagration	Self sustaining internal combustion propagating by means of molecular heat transfer slower than the speed of sound (the explosion mechanism of gunpowder and other ‘low’ explosives)
ΔH°_f	Standard heat of formation
Desiccate	Dry intensively
Detonable	Capable of detonation
Detonation	A self sustaining decomposition reaction propagating faster than the speed of sound by means of a shock wave (the characteristic property of ‘high’ as opposed to ‘low’ explosives).
Diglyme	Diethyleneglycol dimethyl ether
Digol	Diethyleneglycol
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EL	Explosive limits (or Flammable limits), vol% in air
Endotherm	Absorption of heat
ESCA	Electron scanning chemical analysis
Exotherm.	Liberation of (reaction) heat
Freeze drying	Drying without heat by vacuum evaporation of frozen solvent
GLC	Gas-liquid chromatography
Glyme	Ethyleneglycol dimethyl ether
Halocarbon	Partially or fully halogenated hydrocarbon
HMPA	Hexamethylphosphoramide
HMSO	Her Majesty’s Stationery Office
Homologue	Compound of the same (organic) series
Hypergolic	Ignites on contact
Ignition source	A source of energy which ignites flammables
IMS	Industrial methylated spirit (ethanol)
Induction period	Delay in reaction starting, caused by inhibitors
Inorganic	Not containing combined carbon, of mineral origin
Intermolecular	Between different molecules
Intramolecular	Within the same molecule
IR	Infrared spectroscopy
Initiation	Triggering of explosion or decomposition
LAH	Lithium tetrahydroaluminate
Lanthanide	Of the group of rare-earth metals
LRS	Laser Raman spectroscopy

LPG	Liquefied petroleum gas
MAPP	Methylacetylene/propadiene/propene mixture
Molecular sieve	A zeolite lattice with micropores of specific sizes, useful for molecular separations
m.p.	Melting point
MRH	Maximum reaction heat
NMR	Nuclear magnetic resonance spectrosopy
Nomenclature	System of naming chemicals
Off-spec.	Off-specification (low quality)
Oleum	Sulfur trioxide dissolved in sulfuric acid
Organic	A compound containing combined carbon
Organometallic	Containing carbon to metal bonding
Oxidant	Oxidising agent (electron sink)
PCB	Polychlorinated biphenyl
PTFE	Polytetrafluoroethylene
Propagation	Spread or transmission of decomposition, flame or explosion
Propellant	Energetic composition used in ballistics
PVC	Polyvinyl chloride
Pyrophoric	Igniting on contact with air (or frictional sparking)
Q	Heat of (exothermic) reaction or polymerisation
Quaternary salt	Tetra-substituted ammonium salt etc.
RCHD	Reactive Chemical Hazards Database, which you are using, either in book form or electronically
Redox	Reaction or Compound with reducing and oxidising features
Reducant	Reducing agent (electron source)
Refractory	Heat resisting
REITP2	A computer program to calculate MRH
RSC	Reaction Safety Calorimeter, or Royal Society of Chemistry
Runaway	Reaction out of control
Self-accelerating	Reaction catalysed by its own products
Self-heating	When substance generates heat faster than it is dissipated
Silicones	Organic derivatives of a polysiloxane chain
Slurry	Pourable mixture of solid and liquid
Smelt	Molten sodium sulfide and carbonate from evaporated sulfite liquor
Substance	Not a single chemical species, often of natural origin
Superheated	A liquid at a temperature above its boiling point
Tait24	Temperature of adiabatic storage which gives an induction time to exothermic decomposition of 24 hours
Thermite reaction	Reaction of aluminium powder and iron oxide producing molten iron (and analoguous reactions)
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
Thermochemistry	Study of heat effects of chemical reactions
TLC	Thin layer chromatography

TNT	Trinitrotoluene
U	Heat of (exothermic) decomposition
Unit operation	A single operational stage of a chemical process sequence – may be purely physical, e.g. distillation or drying
Unit process	A single chemical reaction stage in a process sequence
USNTIS	US National Technical Information Service
UV	Ultraviolet spectroscopy

Appendix 3

Index of Class, Group and Topic Titles used in Volume 2

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Appendix 4

Index of Section 2 Titles Classified by Type

This Appendix contains the same entries as Appendix 3, but they are classified on the basis of the type of information content, as indicated by the bold section headings. A few titles appear in more than one section.

Many of the chemical classes given immediately below contain lists of their constituent chemical group and sub-group titles, and some of the class titles, (those without page numbers) do not appear in the text, being used only in classifying this Appendix.

Definitions of the chemical class headings are as follows.

Inorganic chemicals don’t contain carbon among the elements present.
Organic chemicals do contain carbon along with other elements.
Organometallic chemicals are organics which contain carbon to metal bonds.
Hybrid chemicals contain structural features of 2 or more of the above.
Performance materials are grouped according to how they behave or perform.
Substances are not single simple chemical entities, often of natural origin.

Hazard Assessment and Prediction; Miscellaneous Topics; Phenomenon Topics; Specific Reaction Hazards; Technique Topics; and **Unit Operations** are less specifically chemical sections.

Technique Topics

How to use the Handbook

To seek

1. **Stability data on single specific compounds:** look in Volume 1 using either the chemical name index (Appendix 4, Volume 1) or the empirical molecular formula at right of second title line (Carbon; then Hydrogen if present; other elements follow alphabetically) to locate the page. Membership of a general group is shown by a *See other*... cross-reference.
2. **Data on possible violent interaction between two or more compounds:** determine which appears "more reactive" and find it as in 1 above. Then look down the sub-entry titles for the other compound(s) involved which may be given as a single compound or as one of a group The latter are listed in Appendices 3 and 4 in Volume 2.
3. **General data on a class or group of compounds, or information on identity of individuals in a known hazardous group:** refer to the Alphabetical Volume 2. There is an alphabetical index to this Volume in Appendix 3, and a classified index in Appendix 4.
4. **Structure associated with explosive instability**: *See* EXPLOSIBILITY
5. **Information on general topics:** use the indexes in Appendix 3 or 4 in Volume 2.
6. **Fire-related data:** this is tabulated in Appendix 2, Volume 1.
7. **Information on a compound identified by its CAS Registry number:** there is a numerical index of CAS numbers *vs* Serial numbers in Appendix 5, Volume 1.

Do not assume that lack of information means that no hazard exists. Look further at related structures, using Appendix 3 or 4, Volume 2.

See rear end paper for **What the handbook provides.**

Readers are encouraged to submit details of new reactive hazards for inclusion in later editions. There is a page you can copy for this purpose at the end of both volumes.

What the Handbook Provides

In Volume 1 information on individual chemicals and the class or group(s) to which each belongs.

⑦ **0056. Aluminium tetrahydroborate (Aluminum borohydride)** ⑯

⑮ **[16962-07-5]** **AlB_3H_{12}** ①

$Al[BH_4]_3$ ②

⑭ 1. Schlessinger, H. I. *et al., J. Amer. Chem. Soc.*, 1940, **62**, 3421
2. Badin, F. J. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 2950

The vapour is spontaneously flammable in air [1], and explodes in oxygen, but only in presence of traces of moisture [2]. ⑥

⑪ Alkenes, Oxygen

Gaylord, 1956, 26

The tetrahydroborate reacts with alkenes and, in presence of oxygen, combustion is initiated even in absence of moisture. Butane explodes after an induction period while butadiene explodes immediately. ⑬

See other INDUCTION PERIOD INCIDENTS

Water MRH 1.72/36 ③

Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 4

Interaction at ambient temperature is explosive.

See other COMPLEX HYDRIDES ④

⑫ **†0596. Tetrafluoroethylene**

[116-14-3] **C_2F_4**

$F_2C{=}CF_2$

KEY:

1. Empirical formula which determines order in text

2. Structural formula

3. Calculated value for maximum reaction heat from the mixture

4. Cross reference to class entry in Volume 2

5. General class or group formula

6. Brief information on the class hazard

7. Full entry in Volume 1, Serial No 0056 is reproduced above

8. Cross reference to a related class

9. List of chemicals and serial numbers in Volume 1 which belong to this class

C_2F_4

In Volume 2, information on classes of group of chemicals with similar structures or hazardous properties with lists of the individual chemicals comprising the class or group.

④ **COMPLEX HYDRIDES** $[MH_n]^-,[EH_n]^-$ ⑤

1. Gaylord, 1956
2. Semenenko, K. N. *et al., Russ. Chem. Rev.*, 1973, 1–13
3. Ashby, E. C., *Rept. AD-A057764*, Richmond (Va.), USNTIS, 1978

This class of highly reactive compound includes several which have found extensive use in preparative chemistry [1]. Properties and reactions of several covalent tetrahydroborates have been reviewed [2]. Preparation and properties of several new hydrides are given which are of interest as high-energy fuels in propellant systems [3]. Individually indexed compounds are: ⑩

* Aluminium dichloride hydride diethyl etherate, 0061
Aluminium tetrahydroborate, 0058
Caesium hexahydroaluminate(3—), 0067
Copper tetrahydroaluminate, 0068
Lithium tetrahydroaluminate, 0075 ⑨
Lithium tetrahydroborate, 0145
Manganese(II) tetrahydrolaluminate, 0086
Potassium hexahydroaluminate, 0077
Sodium tetrahydroaluminate, 0076

See other REDUCANTS *See also* METAL HYDRIDES, NON-METAL HYDRIDES
⑧

* *denotes a chemical with a structure related to that of the class or group. See front end-paper for* **How to use the handbook.**

10. Literature reference to general class hazards. Textbooks (no initials) listed in Appendix 1 (both Volumes)

11. Chemical class or group title, ordered alphabetically, listed in Appendix 3 and classified in Appendix 4 (Volume 2)

12. †The material is of high fire potential, properties tabulated in Appendix 2 (Volume 1)

13. Reference(s) and hazards with other chemicals

14. Reference(s) and hazards of the title material

15. CAS Registry Number. Index in Appendix 5 (Volume 1)

16. Serial no., chemical name and synonym. Index in Appendix 4 (Volume 1)