AN INDEXED GUIDE TO PUBLISHED DATA

Handbook of Reactive Chemical Hazards

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L. BRETHERICK, BSc, CChem, FRSC

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Butterworths
London Boston Durban Singapore Sydney Toronto Wellington

First published 1975
Second edition 1979

British Library Cataloguing in Publication Data

Bretherick, L.
Handbook of reactive chemical hazards. : an
indexed guide to published data.–3rd ed.
1. Hazardous substances 2. Reactivity (Chemistry)
I. Title
541.3'9 T55.3.H3

ISBN 0-408-01388-5

Library of Congress Cataloging in Publication Data

Bretherick, L.
Handbook of reactive chemical hazards.

Bibliography: p.
Includes index.
1. Hazardous substances – Handbooks, manuals, etc.
2. Chemicals – Safety measures – Handbooks, manuals, etc.
I. Title.
T55.3.H3B73 1985 660.2'804 85-7922
ISBN 0-408-01388-5

Computerized typesetting by First Page Ltd., Watford, England

Foreword

During the two years in which I chaired the Enquiry Committee on Safety and Health of people at their place of work, what was certainly borne upon us was the tremendous speed of advance of modern technology and the importance of keeping up to date with the safety factors surrounding new developments.

This handbook, the product of Mr. L. Bretherick, certainly adds a new dimension to this whole problem.

It is very clear from its exposition that every single contingency that can at present be contemplated in the whole field of laboratory safety has been covered, and there is no doubt that from time to time there will require to be reviews in the light of chemical development. Sufficient to say, however, that within these pages lies an enormous amount of research work in this whole area of work in the chemical industry, that there has been collected a tremendous amount of information on hazards in laboratories and that Mr. Bretherick has become recognised as an expert in this field.

Safety Officers who are responsible for safety in industrial laboratories will find this book absolutely essential reading if they are to do their own work to the satisfaction of themselves and of the company which they serve.

I know of no previous book containing so much information as this one, and there is no doubt at all that if the book is diligently used there will be found within its pages answers to many of the problems in relation to safety in the use of chemicals.

I can only say, having spent so much time in the whole field, that the development of the modern technologies is the area in which safety research needs to be constantly updated. In the older industries already there is sufficient information to enable us to conduct our affairs in such a manner as to provide adequate safety and a proper healthy environment for the workers in those fields. It is in the modern fields that the problems arise, because with great frequency there are new discoveries that require fresh thought in relation to safety hazards.

Mr. Bretherick has undoubtedly produced for all those in this field a handbook that will enable the greatest possible safety precautions to accompany the developing sciences. That Mr. Bretherick should have been able to produce what is a monumental contribution to safety is a matter of great credit to him and the enormous amount of research that was required in order to produce this book.

I therefore recommend most strongly a careful survey of the entries in this book relevant to the activities of particular companies in this field, and feel very strongly that Safety Officers require this constantly at their elbow in order to provide the right kind of environment in which work in laboratories can be conducted with greater safety than is possible without the research benefits that have come from this book.

It is absolutely essential in the modern world that safety factors in research must be adequately safeguarded, and this means that the maximum amount of information must be available at all times, based upon present knowledge. It is because I recognise the value of the work that this book embraces in the whole difficult field of modern research and technology, that I unhesitatingly in this foreword make the strongest recommendation for its close attention and use in laboratories.

In our travels as a Committee of Enquiry, we found that many countries in the world look to the United Kingdom for a lead in these matters. This book produces further evidence of the care and attention required in this highly critical area of laboratory research and, therefore, will be welcomed both in the United Kingdom and overseas.

I am certain that as a result of this work a great many people engaged in actual research, and the companies concerned, will find this of considerable help and assistance in safeguarding all those who are engaged in breaking through the frontiers of knowledge.

LORD ROBENS OF WOLDINGHAM

November, 1974

Preface to the Third Edition

The generous decision of my former employers to allow my early retirement from the BP Research Centre in 1982 provided the opportunity for a complete revision and resetting of the second edition to be undertaken, incorporating the new information which has become available since September 1977. Much of this reflects the higher general level of concern to promote the safer use of reactive chemicals in both research and production areas. Title entries for some 4900 compounds are now included.

The general presentation is similar to that of the second edition, but some changes in detail of typography, layout and content have been made to make better use of page space, to simplify use of the information content and to enhance its value to the reader.

The main part of the book, the **Specific Chemical Section** now follows immediately after the preliminary pages, while the **Class, Group and Topic Section** comes second in order. This change was necessary so that page numbers rather than empirical formulae could be used to indicate the location of the individual chemicals of the class and group lists in Section 2. CAS Registry numbers are now included for most of the compounds in Section 1. A further addition to this section is the inclusion of much quantitative information on the energy of decomposition of compounds or mixtures, including both measured and calculated values, as well as the heats of formation of a wide range of endothermic compounds.

The considerable gap in safety information sources on specific chemicals left in 1980 by the total withdrawal of the *MCA Data Sheet* series has largely been filled by the continuing series of *National Safety Council* and *Fire Protection Association* Data Sheets, as well as by *Handling Chemicals Safely 1980* and the new *RSC Laboratory Hazard Data Sheets*. Concise references to all these sources of general handling precautions are now included under the title lines in Section 1.

There are some 500 group and topic titles in Section 2, now including some which bring together incidents involving the same physical cause or effect, but different types of chemical materials. The compound lists present in about half of the group and class entries are now much more extensive, being compiled by automatic computer searching techniques applied to the whole text of Section 1. Upper and lower case letters have been used throughout for all chemical names in titles, text and compound lists, small capitals now only being used for references in Section 1 to the group, class and topic titles of Section 2.

The task of locating suitable current material for this book has been greatly lightened by the selected abstracts *Chemical Hazards, Health, & Safety* emanating from Chemical Abstracts Service, and by *Laboratory Hazards Bulletin* and *Chemical Hazards in Industry* now available from the Royal Society of Chemistry. The continuing publications of the Institution of Chemical Engineers and the Chemical Industries Association in the UK, of the Berufsgenossenschaft in Germany and of the ACS Chemical Health & Safety Division in the USA (notably those of Howard H. Fawcett and Professor Malcolm M. Renfrew), have also yielded well. Professor Tadao Yoshida of the University of Tokyo has kindly allowed the use of many of the calculated values of maximum energy release for binary mixtures, taken from his *Handbook of Hazardous Reactions with Chemicals*.

I am again indebted to the British Petroleum Company, p.l.c., and also to Royal Holloway College, University of London for the use of library facilities. It is a particular pleasure to record the greatly increased number of concerned people who have voluntarily supplied information for inclusion as private communications, in addition to those individuals or companies, both in the UK and overseas, who have generously responded to my requests for information or additional information. The contributions made to previous editions by those not now individually named here are also remembered with gratitude.

My thanks are due to Dr E. R. Smith of the Chemical Society for help with IUPAC nomenclature problems, to the editorial staff at Butterworths, to First Page Ltd. for much help and advice on word processing and related matters, and to Sofis Systems Ltd. for the bug-free text searching programs.

None of the considerable and sustained effort during the past 20 years would have been possible without the continuing support and encouragement of my wife. To her I dedicate this work.

L.B.

February 1985

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.

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 selection of documented information to research students, practising chemists, safety officers and others concerned with the safe handling 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 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 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 author by December 1984 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 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 Kirk-Othmer in the industrial area). Section 50 of *Chemical Abstracts*, the CAS selection *Chemical Hazards, Health, & Safety*, the *Universities' Safety Association Safety News*, the CIA *CISHC Chemical Safety Summary* and the IChE *Loss Prevention Bulletin* have been rich sources, together with the 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 all the sources used are set out in Appendix 1. References in the text to textbooks are characterised by absence of the author's initials.

Information on toxic hazards has been specifically excluded because it is available elswhere 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, with possible toxic effects, either acute or chronic. Also, 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 any 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 highly flammable substances, some 550 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 limits in air where known are given in the tabular Appendix 2. Those elements or compounds which ignite on exposure to air are also included in the text.

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 sections 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 Section 1 of the Handbook. For an example of an unstable compound,
See Ethyl perchlorate, p. 276
For an example of a hazardous interaction between 2 compounds,
See Nitric acid: Acetone, p. 1101
or 2 separate examples involving the same compound,
See Nitric acid: Acetone, or: Ethanol, pp. 1101, 1103

and one involving 3 compounds,

See Hydrogen peroxide: Nitric acid, Thiourea, p. 1160

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

See ACYL NITRATES, p. 1424
PYROPHORIC METALS, p. 1673

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 now given in normal roman typeface.

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

See BLEACHING POWDER, CELLULOSE NITRATE, pp. 1461, 1467

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

See DISPOSAL, EXPLOSIBILITY, pp. 1501, 1511
GAS CYLINDERS, OXYGEN ENRICHMENT, pp. 1522, 1636

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

See CATALYTIC IMPURITY INCIDENTS, p. 1465
GAS EVOLUTION INCIDENTS, p. 1522

Specific Chemical Entries (Section 1)

A single unstable compound of known composition is placed in the main first section 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. 212

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. 1179
Iodine: Ammonia, p. 1227

are referred back to the main entry under the identified material

Nitrogen triiodide–ammonia, p. 1231

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.1242

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. 43

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. 132

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. 1355

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. 292
Acetyl chloride: Dimethyl sulfoxide (back reference), p. 240

Grouping of Reactants

There are advantages to be gained in grouping together elements or compounds showing similar reactivities, 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. 953
Hydrogen peroxide: Metals, Metal oxides, Metal salts, p. 1158
Hydrogen sulfide: Oxidants, p. 1172

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 group titles listed in Appendix 5 will be of use in this connection.

General Group Entries (Section 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 Section 2.

Cross references to related group or sub-group entries are also included, with a group list of the names and page numbers of the chemicals appearing in Section 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 Section 1 of this Handbook.

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 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 been used occasionally 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 in 1972 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 (Appendix 4). 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 Section 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.

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 strict analogues of the compound etc.

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

See entry... points to a relevant reference elsewhere.

Information content of individual entries

A conscious effort has been made throughout this compilation to exclude all fringe information not directly relevant to the involvement of chemical reactivity in the various incidents or observations, with just enough detail present 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 available, *before* attempting any experimental work with materials known, or suspected, to be hazardous or potentially so.

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.

One aspect which, although it is excluded 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. 1463), others have involved personal injuries, often of unexpected severity (*see* SODIUM PRESS, p. 1691), and material damage is often immense. For example, the incident given under Perchloric acid: Cellulose derivatives, (reference 1, p. 909) 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. 213) to some 600 with 2000 injured in the incident at Oppau in 1923 (*see* Ammonium nitrate, reference 4, p. 1195), and now to over 2,500 with more than 100,000 injured by methyl isocyanate fumes at Bhopal in 1984.

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.