DESTRUCTION OF HAZARDOUS CHEMICALS IN THE LABORATORY

Second Edition

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Preface

This is the second edition of *Destruction of Hazardous Chemicals in the Laboratory*, originally published in 1990. Most of the existing monographs have been modified to a greater or lesser extent to take into account recent developments in the literature. Entirely new monographs have been included on the removal of metal ions (including lead, mercury, and uranium) and biological stains from solution and the degradation of mycotoxins, enzyme inhibitors (including diisopropyl fluorophosphate and phenylmethylsulfonyl fluoride), polycyclic heterocyclic hydrocarbons, and highly reactive reagents, such as butyllithium, chlorosulfonic acid, peracids, and phosgene.

Hazardous materials, such as complex metal hydrides, are frequently used to prepare super-dry solvents. So as to provide alternatives to these materials we have added a review on the use of much less hazardous reagents, such as molecular sieves (Appendix II). In recent years a number of technologies have begun to emerge that show great promise for treating the complex waste streams produced by biomedical research institutions. Dr. Steven W. Rhodes has contributed an overview of developments in this field, which is included as "Emerging Technologies Applicable to the Treatment of Hazardous Waste in Biomedical Research Institutions" (Appendix IV).

The format is essentially the same as that previously used, although CAS Registry Numbers have now been added at appropriate places in the Monographs.

As before, this book is a collection of detailed procedures that can be used to degrade and dispose of a wide variety of hazardous chemicals. The

procedures are applicable to the amounts of material typically found in the chemical laboratory. Exotic reagents and special apparatus are not required: The procedures can readily be carried out, often by technicians, in the laboratory where the hazardous materials are used.

Bulk quantities of hazardous materials and solutions in various solvents can also be degraded using the procedures described in this book. Methods for cleaning up spills are frequently indicated, as are solvents for wipe tests to ensure complete surface decontamination. A listing of hazardous compounds, indexed by name, molecular formula, and CAS Registry Number provides ready access to the information.

The safe handling and disposal of hazardous chemicals is an essential requirement for working with these substances. We hope that this book will contribute to encouraging the use of tested and sound practices.

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March, 1994

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We wish to thank Dr. Steven W. Rhodes for providing the review of emerging technologies applicable to the treatment of hazardous waste in biomedical research institutions (Appendix IV).

Contents

INTRODUCTION

Biological agents can be completely inactivated by treating them with formaldehyde, ethylene oxide or moist heat, and radioactive materials will decay with the passage of sufficient time, but there are no general destruction techniques that are applicable to chemical agents. The availability of destruction techniques for hazardous chemical agents would be particularly helpful because of the dangers associated with their handling and disposal. In addition, being able to destroy or inactivate the hazardous materials where they are used is advantageous because the user should be familiar with the hazards of these materials and the precautions required in their handling.

Here we present summaries of destruction procedures for a variety of hazardous chemicals. Most of the procedures have been validated, many by international collaborative testing. We have drawn on information available in the literature[1–13] and on our own published and unpublished work.

About This Book

This book is a collection of techniques for destroying a variety of hazardous chemicals. It is intended for those whose knowledge of the chemistry of the compounds covered is rather sophisticated; that is, for those who are aware not only of the obvious dangers, such as the toxic effects of the compounds themselves and of some of the reagents used in the methods, but also of the potential hazards represented, for example, by the possible

formation of diazoalkanes when *N*-nitrosamides are treated with base. If you are not thoroughly familiar with the potential hazards and the chemistry of the materials to be destroyed and the reagents to be used, do not proceed.

The destruction methods are organized in what we believe to be rational categories. These categories are listed in the Table of Contents. It is quite likely, however, that others would have categorized these methods differently, so we have provided three indexes. We have assembled many synonyms of the compounds covered into a Name Index. In each case, the page number given is the first page of the monograph in which the destruction of that compound is discussed. In some cases, the compound itself may not have been studied; it may have been referred to in the Related Compounds section. Since it is not possible to cite every synonym and every variation in spelling, we have also provided a CAS Registry Number Index and a Molecular Formula Index. With these aids one should be able to find the appropriate destruction method for the compound in question. As a further aid, recognizing the fact that frequently a destruction method is sought only after an accident occurs, we have added an appendix that lists the solvents recommended for use with wipes that are used to sample the area where a spill has occurred in order to determine whether the cleanup has been complete.

One of the difficulties in preparing a book such as this is deciding what should be included and what should be excluded from the text. We have tried to make the method descriptions and the supporting references complete, but at the same time not include unnecessary details. We also tried to eliminate ambiguity wherever possible, going so far as to repeat almost verbatim certain procedures for some compounds rather than noting a minor change and referring to another section and risk a wrong page number or a misinterpretation. Some general safety precautions are given below. These are not repeated for each group of compounds; in some cases, unusual hazards are noted. For many of the destruction procedures we use the word "discard" in connection with the final reaction mixture. This *always* means "discard in compliance with all applicable regulations."

Although we have included all the validated destruction procedures known to us, we realize that there may be other procedures in the literature. Thus, we would be pleased to hear from readers who have any information or suggestions. This work is continuing and we would also be pleased to hear from readers who have suggestions for future work or other comments.

Properties of a Destruction Technique

We have already indicated the advantages of destroying hazardous chemicals at the place where they were generated. It is also useful to consider the desirable properties of a destruction technique.

- Destruction of the hazardous chemical should be complete.
- A substantially complete material accountance should be available, with the detectable products being innocuous materials. (This accountance is often difficult to accomplish. In the absence of a complete material accountance, an assessment of the mutagenic activity of the reaction mixture may provide useful information concerning the potential biological hazards associated with the decomposition products.)
- The effectiveness of the technique should be easy to verify analytically.
- The equipment and reagents required should be readily available, inexpensive, and easy and safe to use. The reagents should have no shelf-life limitations.
- The destruction technique should require no elaborate operations (such as distillation or extraction) that might be difficult to contain; it must be easy to perform reliably and should require little time.
- The method should be applicable to the real world; that is, it should be capable of destroying the compound itself, solutions in various solvents, and spills.

These properties characterize an ideal destruction technique. Most techniques cannot meet all of these criteria, but they represent a goal toward which one should strive.

Contents of a Monograph

Each monograph usually contains the following information:

- An introduction describes the various properties of the compound or class of compounds being considered.
- The principles of destruction section details, in general terms, the chemistry of the destruction procedures, the products, and the efficiency of destruction.

- The destruction procedures section may be subdivided into procedures for bulk quantities, solutions in water, organic solvents, and so on.
- The analytical procedures section describes one or more procedures that may be used to test the final reaction mixtures to ensure that the compound has been completely degraded. The techniques usually involve packed column gas chromatography (GC) or reverse phase high-performance liquid chromatography (HPLC), but colorimetric procedures and thin-layer chromatography (TLC) are also used in some cases.
- The mutagenicity assays section describes the data available on the mutagenic activity of the starting materials, possible degradation products, and final reaction mixtures. The data were generally obtained from the plate incorporation technique of the *Salmonella*/mammalian microsome mutagenicity assay (see below).
- The related compounds section describes other compounds to which the destruction procedures should be applicable. The destruction procedures have not usually been validated for these materials, however; they should be fully investigated before adopting them.
- References identify the sources of the information given in the monograph.

Mutagenicity Assays

The residues produced by the destruction methods were tested for mutagenicity. Unless otherwise specified, the reaction mixtures from the destruction procedures and some of the starting materials and products were tested for mutagenicity using the plate incorporation technique of the *Salmonella*/mammalian microsome assay essentially as recommended by Ames et al.[14] with the modifications of Andrews et al.[15] Some or all of the tester strains TA98, TA100, TA1530, TA1535, TA1537, and TA1538 of *Salmonella typhimurium* were used with and without S9 rat liver microsomal activation. The reaction mixtures were neutralized before testing. In general, basic reaction mixtures were neutralized by adding acetic acid. Acidic reaction mixtures were neutralized by adding solid sodium bicarbonate. Reaction mixtures containing potassium permanganate were decolorized with sodium ascorbate before neutralization. A 100 μL aliquot of the solution (corresponding to varying amounts of undegraded material) was used per plate. Pure compounds were generally tested at a level of 1

mg per plate in either dimethyl sulfoxide (DMSO) or aqueous solution. To each plate were added 100 μL of these solutions. The criterion for significant mutagenicity was set at more than twice the level of the control value. The control value was the average of the cells only and cells plus solvent runs. Unless otherwise specified, residues did not exhibit mutagenic activity. The absence of mutagenic activity in the residual solutions, however, does not necessarily imply that they are nontoxic or have no other adverse biological or environmental effects.

Analytical Procedures

Unless otherwise specified the analytical equipment used in our work consisted of the following. For HPLC a dual pump computer-controlled solvent delivery system (Rainin Instrument Co., Woburn, MA) was used with ultraviolet (UV) detection using either a Knauer Model 87 variable wavelength detector (Rainin) or an ABI 1000S diode array detector (Applied Biosystems, Foster City, CA). The injection volume was 20 μL and the flow rate was 1 mL/min. The column was a 250 × 4.6-mm i.d. column of Microsorb 5 μm C8 fitted with a 15 × 4.6-mm guard column of the same material. For GC a Hewlett Packard HP 5880A instrument was fitted with a 1.8-m × 2-mm i.d. × 0.25-in. o.d. packed silanized glass column. The column was fitted with a guard column packed with the same material. The guard column was changed periodically. The injector temperature was 200°C and the flame ionization detector temperature was 300°C. The carrier gas was nitrogen flowing at 30 mL/min. Injection was by syringe and sample volumes were in the 1–5-μL range. For each instrument an electronic integrator was used to determine peak areas automatically.

In some cases we found that injecting unneutralized reaction mixtures onto the hot GC column caused degradation of the material for which we were analyzing. Thus it might be that degradation was incomplete but the appropriate peak was not observed in the chromatogram because the compound was degraded on the GC column. Spiking experiments can be used to determine if this is a problem. In a spiking experiment a small amount of the original compound is added to the final reaction mixture and this spiked mixture is analyzed. If an appropriate peak is observed, compound degradation on the GC column is not a problem. If an appropriate peak is not observed, it may be necessary to neutralize the reaction mixture before analysis and/or use a different GC column. Similar problems may