Chemical Process Hazard Review

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Chemical Process Hazard Review

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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

PREFACE

ASSURANCES THAT NEW AND EXISTING CHEMICAL PROCESSES are conducted safely have never been more needed. Public awareness of the effects of chemical exposure has increased since the early 1970s. Although the initial focus of the Occupational Safety and Health Act of 1970 was on safety, clearly the emphasis now is on health. People at all levels of society are concerned about exposure to chemicals and the possible short- and long-term effects of chemicals on human health. The effects of chemicals on the environment from past or present waste sites, accidental releases or spills, and fires and explosions are reported daily in the news media. Control of all chemical processes to avoid accidental discharges and/or upsets that lead to fires, explosions, and environmental release is essential in the laboratory, the pilot plant, and the manufacturing plant. Chemical process hazard reviews are necessary at each step in the development of a process to ensure that the process can be controlled and conducted so as to minimize the risks to personnel, property, and the environment.

The purpose of the symposium upon which this book is based was to provide a forum for the exchange of information on chemical process hazards reviews by industrial research and development chemists, chemical engineers, and safety professionals. The chapters in this text are representative of the subjects presented at the symposium and are provided to give wider dissemination and availability of this information.

We are indebted to the executive committees of the ACS Health and Safety Division and the NSC Industrial Division Chemical Section for their interest and support. A special thanks to each of the authors for their timeliness and, more important, their willingness to take time out of their schedules to share their knowledge and experience with others. Finally, we must acknowledge the Warner-Lambert Company, Parke-Davis Division, for continued support, materially and philosophically.

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Chemical Process Hazard Review

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The phrase Chemical Process Hazard Review has widely varying meanings. To the professional safety engineer, it connotes a broadly based review of a chemical process which when conducted properly would provide assurances that a process can be conducted "safely"; safe for the scientists in the laboratory, the technician in the pilot plant and the chemical operators in the manufacturing plant. The developing chemist may view a chemical process hazard review as just another hurdle to jump enroute to getting his/her process into the pilot plant or manufacturing plant. Chemical engineers destined to design both the process and equipment may depend on such a review to provide the details necessary to design the process "safely." Environmental engineers and control specialists consider a review process as a means for estimating risk to environmental exposure (air, water and ground) and a source of data to develop compliance information. Management needs the assurance from both line managers and staff functions that the process can be conducted and the hazards associated with that process in its entirety are identified to the extent that appropriate risk/benefit decisions can be made. An appropriate Chemical Process Hazard Review can and should meet all of these needs.

Life in the chemical process development world is no longer one shrouded in the mysteries that synthetic organic chemistry can present. The basic researcher does not have the luxury of living in

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an isolated laboratory and day after day producing new chemical entities through ever increasing complex chemistry without regard to the ultimate process in the pilot plant. The developmental chemist's concern is not just defining a workable, cost-effective process but one which can be done "safely" and economically. The chemical engineer designing a plant scale process also has added a number of new concerns which must be considered before committing to a plant installation.

Consider for a moment just the changes in vocabulary during the past twenty years among these professions. Chemists and chemical engineers long known for their seemingly capricious use of acronyms and peculiar jargon are faced with incorporating and understanding those invented and used by others. OSHA, PEL, NIOSH, RTECS, HMTA, FWPCA, CPSA, IARC, FEPCA and SF are just a few. With this seemingly overwhelming burden of regulatory requirements, life and business must go on and they are. A small part of continuing life and business has been and is in the Chemical Process Hazard Review.

Notwithstanding the complexities considered above, chemical processes must be developed in a way which people, the environment and property are protected. The chemical reaction process itself presents its own peculiar evaluation needs which impact upon occupational safety and health, environmental protection and property preservation and conservation. In the progression of a process from the research laboratory to the development laboratory to the pilot plant and eventually to manufacturing, the objectives for the process review must be:

1. The ability to carry out the desired process producing the desired products, profitably;
2. Development of data which can characterize the reaction, including side or minor products, and the conditions under which they may be produced.
3. Development of reaction conditions (temperatures, pressure, concentrations and equipment) at which the process can be conducted "safely."
4. Identification of conditions and events (other than normal) which can lead to hazardous conditions or products.

Most major chemical and pharmaceutical companies today have developed systematic methods of evaluating new (and in many cases, old) processes and materials for the hazards attendant to their manufacture. The degree of urgency in establishing a chemical process hazard analysis function has often been dictated by some untoward event (usually within the company). It is to the prediction and control or elimination of unplanned reaction events to which the chemical process hazard review must address itself.

Broadly, the review process can be segregated into: an understanding of the chemistry, desired and possible; a thorough literature review of related chemical reactions and processes; theroretical calculations; and design and conduct of experiments to confirm hypotheses and/or gather additional data.

Process Chemistry

In understanding the desired and possible chemistry the process at each step should be categorized as to type of reaction and a balanced chemical equation developed. The use of a broad categorization such as given in Table I is frequently used as a starting point. All probable side products should be identified and their potential role(s) postulated. Rate determining steps in multi-step or sequential processes should be so labeled and their import to the process identified.

Table I. Chemical Reaction Energy Categorization

Process	Energy	Chemical Hazard Potential
Oxidation	Highly Exothermic Equilibrium Favored	High
Nitration	Exothermic Potential oxidation	High
Reductions	Low	Low
Halogenations	Highly Exothermic chain reaction for Chlorine & Fluorine	High
Sulfonations	Moderately exothermic	Low
Hydrolysis	Mildly exothermic	Low
Polymerization	Can be highly exothermic	Moderate to high
Condensations	Moderately exothermic	Low to moderate
Hydrogenation	Mild to moderately exothermic easily controlled	Moderate to low
Alkylation	Mildly exothermic side reactions generally a problem	Low
Organo Metalics	Highly exothermic	High
Amination	Moderately exothermic	Low

Identification and quantification of the desired reaction conditions, particularly temperature and concentration, are necessary to evaluate what may happen if these conditions are not met. This is particularly true where equilibrium considerations are a significant factor in a rate determining step between or among competing reactions. Where multiple products are possible, temperature variations will often significantly alter the ratios of these products. If one of these is unstable or more toxic, this could lead to more stringent temperature control requirements in the process and equipment design.

Identifying the "type" of reaction can be useful in broadly categorizing the overall potential hazards as well as aiding in the literature search. Many literature sources refer to reactions not only by their historical name but also by their type. If a reaction step in a process can be identified in this manner, it may aid in the literature search and in keying various reviewers memories. Types of reactions such as Fridel-Crafts, Grignard, Meerwin-Ponndorf, Cannizzaro, Clemenson. Wolff-Kishner, Hofmann Degredation, Beckman Rearrangement, Simmons-Smith, Piels-Alder, Wurtz-Fitig, etc. may not be household names to everyone, but they are to many organic chemists. More importantly, literature sources can be searched for these classifications to give an overall perspective to a reaction under study.

Literature

Not enough can be said about literature reviews when you consider how many chemists there are in the world today (128,000 current members in the American Chemical Society alone) and when you consider how many there have been from the days of Priestly, the number is awesome. Many of these chemists as experimentalists have tried mixing a little of everything with anything to see what would happen. Often something dramatic did happen. Much of this information has been recorded in the literature albeit a bit hard to find at times. Frequently, chemical accidents in the laboratory are reported in C&E News in the letters to the editor. Invariably, after publishing the untoward event in this manner other readers will respond with reports of similar occurences that they were involved in or knew about. And others will report a like event recorded in the literature in years past. Table II lists a few starting points for literature reviews. As is often the case in literature searches, one key article can often provide the route back to previous authors and reviewers who have worked in that particular area of chemistry.

Table II. Literature Review

- L. Bretherick - Hand Book of Reactive Chemical Hazards
- NFPA 491 M & 49
- Factory Mutual Data Sheets 7-19, 7-23
- Kirk-Othmer
- CMA (MCA) Accident Case Histories Volumes 1-4
- Open Literature Via Chemical Abstracts
- Data Bases Such As:
  Med Lars, Tox Line
  Toxicology Data Bank
  and D D C.

Theoretical Calculations

Theoretical calculations can be made regarding the energy which is available from a reaction. The use of chemical thermodynamic tables, tables of heats of formation and known heats of reaction

can lead to estimations of the energy available. Coupling this with reaction conditions (temperature particularly) and gross rates observed on bench-scale experiments can produce meaningful parameters translatable to scale-up.

Calculations of oxygen balance either for the total reaction mixture or for individual products is a simple yet very effective first-order evaluation of a process or material, particularly nitrations and nitro-containing compounds. Most authors recommend determining the ratio of oxygen available within the system to theoretical oxygen requirements necessary to oxidize all carbon to carbon dioxide, all hydrogen to water, and nitrogen reduced (or in some cases, oxidized) to elemental nitrogen. If other oxidizable species are present, such as sulfur or alkali/alkaline earth metals, these would also be presumed to be oxidized to their oxides in the most stable oxidation state.

The CHETAH Program from ASTM Committee E-27 is also quite useful for theoretical calculations of enthalpy (decomposition, oxidation or combustion), oxygen balance, and potential energy release. Recent modifications of the program and updating of the data base make it even more useful.

Testing

Evaluation of a material or process by analytical tests and experiments is, of course, a must when history (literature), theory and paper chemistry are insufficient to characterize the process or answer the significant "what ifs." Table III lists some of the more common useful methods.

Table III. Testing Methods

DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
TGA	Thermo Gravimetric Analysis
ARC	Accelerating Rate Calorimetry
BSC	Bench Scale, Heat Flow Calorimetry
SEDEX	Sensitive Detector of Exothermic Processes
Others	Oven Tests, Dewar Tests, Hot Plate Tests, etc.

The ultimate purpose of these types of tests is to evaluate two similar (in results) but different occurrences. These are runaway chemical reactions and exothermic chemical decompositions. The first may actually just be a desired reaction out of control while the second is an undesired reaction out of control. Among the purposes which analytical tests serve are the determination of the "onset" of exothermic (endothermic) decomposition. While frequently a specific temperature is cited for such "onsets," one must remember that this temperature is highly dependent on instrument sensitivity, degree of adiabaticity and time-temperature history. It should be stated that tests results are accurate only for the exact conditions under which they were run. Physical factors such as density and geometry can also influence test data. In theory, reaction rates are not a step function but are continuous. A reaction rate for a process is not zero below a given "onset"

temperature, but is merely a smaller number which instrumentation is not sufficiently sensitive to measure. In practice, however, established temperature onsets for process reactions will usually allow a sufficient margin of safety, provided that adequate cooling capability or inherent heat sinks are sufficient to remove heat energy in excess of that which can be generated. For highly exothermic reactions or reactions with low activation energies, it may be necessary to modify the process. Continuous or semi-batch versus batch is one way in which control may be maintained within engineering limits.

Summary

The challenge that faces chemical researchers, development chemists and engineers, manufacturing chemists and engineers and the staff functional professionals associated with chemical processes is formidible. It is one that requires more and better information about chemical processes to meet today's regulatory demands and both public and private expectations for the chemical and pharmaceutical industries. Organized and systematic chemical process hazard reviews are necessary to meet these demands.

The attempt in organizing the Symposium on Chemical Process Hazard Review at the Spring 1984 ACS national meeting in St. Louis, was to present papers on the review procedure, some of the thermochemical evaluation techniques and the application of both of these to actual processes. Some of the papers presented at the symposium have been collected and are published here to further exchange information related to conducting chemical processes "safely."

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Process Hazard Review in a Chemical Research Environment

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The objectives of the Process Hazards Review program at the Du Pont Experimental Station are reviewed. The scope, organization, format, review method, final report, and frequency are discussed as they apply to research projects. The concept of tailoring the review method to the degree of hazard involved is explained and an example of a Process Hazards Review and a Pre-Startup Review/Process Hazards Audit are given.

It has long been recognized that accidents rarely result from unforeseeable hazards. They also rarely come about from "acts of God". What we have come to realize is that accidents really result from a failure to define and control known hazards that exist due to the equipment, the chemicals, the chemistry, or the people involved.

In the Du Pont Company as a whole, a vigorous program of process hazards management, of which Process Hazards Reviews (PHR's) are but one element, was instituted and has been recommended by our Corporate Safety & Fire Protection Division as far back as 1966 (1).

The program, of course, has been widely used at manufacturing sites, but its rigorous application to the research environment in DuPont has been fairly recent - since 1979 (3). In a number of ways, it is still evolving; such as how often should a PHR be held or when is one needed?

Research at the Du Pont Company's Experimental Station encompasses virtually all fields of science - physics, chemistry, biochemistry, and engineering. The scope of experimentation will range from the micro-level, to the semiworks-level, using from milliliter quantities to a drum lot daily. The frequency of experimentation may range from a one-time run in a hood to a round-the-clock operation in a barricade. A Process Hazards Review program must encompass all these possibilities.

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Objectives

The ultimate objectives of the Du Pont Company's Process Hazards Reviews, and Pre-Startup Reviews/Process Hazards Audits, are to:

- eliminate injuries, and
- minimize property and environmental damage resulting from the process hazards.

This is done by:

- Identifying process and equipment hazards which could cause serious injuries, explosions, fires, or toxic material releases. These hazards may have been previously unrecognized; or they may have been recognized and tolerated but avoided by skilled or experienced employees.

- Evaluating the size or impact of the hazards, the potential for injury to personnel and property loss, and the frequency of occurrence,

- Developing recommendations to eliminate or control the hazards, and

- Implementing the recommendations.

Definitions

The terms Process Hazards Review and Pre-Startup Review/Process Hazards Audit have been mentioned and are defined.

Process Hazards Reviews comprise formal committee meetings where hours are spent intensively examining, by one of the methods described later, a chemical reaction or process, with a report, documentation, and follow-up. Pre-Startup Reviews/Process Hazards Audits are no less intensive, but the time spent is less, because the complexity of the process or equipment being examined is less. Reports, documentation, and follow-up are also a part of the Pre-Startup Review/Process Hazards Audit. An equipment acceptance safety inspection would be considered a Process Hazards Audit.

Scope

It is necessary to have an intensive and yet systematic examination of the process or the equipment for hazardous exposures to personnel and to property. This should be held from both a theoretical and a practical view. "What if?" situations or those not readily apparent, such as impurities in reactants, the materials of construction, or the suitability of control devices need to be emphasized.

We have made Process Hazards Reviews and Audits distinct from incident or accident investigations, although either of these

may bring home the need to hold one, as may an area safety audit or survey.

An example where there was a need for a Process Hazards Review occurred recently in investigating an incident in which there was a small explosion in an oxygen supply connection to a high pressure reactor. During the investigation, it was brought out that the oxygen supply system was installed after the original Process Hazards Review was held, and that this new oxygen system had never been intensively reviewed.

Review Needed

The most difficult decision in the research environment is when to conduct a Process Hazards Review. A PHR certainly need not be held for a laboratory-scale experiment conducted in a chemical fume hood following a documented procedure - this is the one end of the spectrum. At the other end, a PHR must be held on a semiworks operation, that will be running around the clock, involving drum quantities of materials. It is in the scale in between that a decision is more difficult. The Du Pont Experimental Station has set up certain guidelines. PHR's must be held on:

- All new capital projects when specified in the project write-up. These capital projects could cover, for example, the purchase and installation of a piece of analytical equipment such as an electron microscope, or the renovation and equipping of a new polymer testing laboratory.

- All Class IV lasers. These are high power lasers having 5×10^{-1} watts of power or greater. PHR's are required because of the control measures, such as interlocks and signs; and the health hazards that exist when these lasers are in use.

Process Hazards Reviews are strongly recommended in these cases:

- New or revised operations in a semiworks area,

- Laboratory reactions that may be potentially explosive because of the reactants or products,

- Laboratory reactions using chemicals that are:

  - highly toxic
  - radioactive
  - carcinogenic

- Laboratory operations on a large scale such as those using 22-liter flasks for reactions, isolations, purifications, etc.,

- Laboratory reactions that will be running around the clock or for more than the normal eight-hour work day, and

- Laboratory operations where standard glassware or plastic will be under pressure.

These guidelines are not meant to be all inclusive and there are cases where a combination of less hazardous conditions can create a need for a Process Hazards Review or a Pre-Startup Review/Process Hazards Audit.

Types of Reviews

The next decision to be made after the need for a PHR has been established is what type of review to hold. A look at the various types and a description of each will be helpful.

- "What if?"

The "What if?" is designed for relatively uncomplicated processes. At each step in the process or reaction "What if?" questions are asked and the answers are considered in evaluating the effects of failures of components or errors in the procedure (2).

- Checklist

For slightly more complex processes, the checklist method provides a more organized approach (2). This is accomplished by the use of lists of words or phrases that will stimulate questions concerning the subject. For example, the phrase Personnel Protection should lead to questions relating to the adequacy of ventilation and toxicity of the chemicals used. There are a number of checklists available in Du Pont, each applicable to the site or department for which it was written. Assignments of certain aspects of the project under review can be made to committee members who have the greatest expertise in that area.

- Failure Mode and Effect Analysis (FM&E)

When analysis is needed of a small portion of a large process or of an item of equipment, such as a reactor, the Failure Mode and Effect method can be used (2). While this method may not evaluate operating procedure errors or omissions, or the possibility or probability of operator error, it does assess the consequences of component failures on the process. This type of analysis has been used infrequently at the Experimental Station, and then most often in a somewhat modified form.

- Hazard and Operability (HAZOP) Study

In this method, every part of a process is examined to