Journal of Thermal Analysis, Vol. 49 (1997) 1609-1616

Hazards

IDENTIFYING HAZARDOUS CHEMICAL REACTIVITY
A brief introduction

E. Donoghue

Process Development Section, Agricultural Products Research Division, American Cyanamid Company, P. O. Box 400, Princeton, NJ 08543–0400, USA

Abstract

Hazardous chemical reactivity is chemical reaction that can produce detonation, deflagration or runaway reaction, which can possibly lead to thermal explosion. In the course of the development of a chemical manufacturing process, the raw materials, process streams, isolated intermediates, final product (and the variations of these that are likely to be caused by some process upset) must all be evaluated to determine the potential of each for hazardous chemical reactivity. Although toxic, ecotoxic and flammability hazards may also result from reactivity, this short article is limited to a review of the general strategy and thermal analytical methods used to identify hazards due to the rapid and uncontrolled release of energy by reaction. It is intended as an introduction to the field, and so provides numerous references to the basic sources.

Keywords: adiabatic calorimetry, differential scanning calorimetry, process safety, reaction calorimetry, reactive chemical hazards

Introduction

The attributes of chemical reaction that may make it hazardous are: (1) the dissipation of a large amount of heat, (2) the generation of a large amount of volatile reaction products, (3) rapid kinetics, and (4) an environment that prevents heat and matter from escaping from the reaction mass. Chemical reactions whose hazard must be considered include the desired reactions, the ones that make up the synthetic pathway to the final product, and undesired reactions that can occur in any of the starting materials, process streams, isolated intermediates or final product. The undesired reactions include (possibly autocatalytic) thermal degradations or polymerizations initiated by higher temperatures, and also reactions that result from mischarging, reverse addition, catalysis by contaminants, reaction with contaminants, etc. Reactivity is not hazardous unless a large amount of heat is generated and/or a large mass of volatiles are produced. Gassy or moderately energetic reac-

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

tions may not be hazardous if their kinetics are slow or heat and volatile products can readily escape. If the total energy released by a material is sufficiently large, the material will have the potential to explode, almost independently of its environment or the kinetics of the individual reactions. If only a moderate amount of energy is released and/or the kinetics are only moderately fast, it is the environment of the reaction mass that determines whether reaction results in explosion. In fact, a spectrum exists: as energy increases, for given kinetics, the potential to explode becomes increasingly independent of the surroundings.

The equipment (reaction vessel, tank for storage or transportation, pipe, condenser, laboratory glassware, etc.) containing the reaction mass can therefore have a decisive effect on hazards potential. The reaction mass is said to be held *adiabatically* if no heat can be exchanged with the surroundings. This is in contrast to the situation where heat is readily exchanged with the surroundings, so that the reaction mass is held *isothermally*, its temperature equal to that of the surroundings. Adiabatic conditions exist to a very good approximation in insulated or very large and unstirred plant equipment (such as a large storage tank), while near-isothermal conditions exist in laboratory glassware that is stirred and in contact with a bath. Near-adiabatic conditions can prevail in any apparatus when reaction kinetics are sufficiently rapid. The environment of the reaction mass is said to be *closed* if matter cannot enter or leave; otherwise, it is *open*. If a reaction mass is held adiabatically, any heat dissipated by reaction will increase its temperature, while if a reaction mass is closed, any volatiles produced by reaction will increase the hydrostatic pressure in the containment vessel.

If heat is released by reaction faster than it is transported to the surroundings, the temperature of the reaction mass will increase. This is *self-heating*. Self-heating is maximal under adiabatic conditions. According to the Arrhenius Rate Law, the rate of a reaction increases exponentially with temperature. As a result, for a given exothermic reaction, the rate at which heat is released increases exponentially with temperature. Therefore, self-heating in an adiabatic environment always accelerates. It eventually achieves a maximum rate of reaction when reactant depletion becomes significant and thereafter slows the self-heating rate. Two important experimental measures of reaction hazard are defined for runaway reaction in adiabatic systems. The *adiabatic temperature rise* due to an exothermic reaction is the maximum temperature increase that can be produced by the enthalpy of reaction. The *time to maximum rate of reaction* is the time required for adiabatic self-heating to accelerate to a maximum from a given temperature.

Hazards due to uncontrolled chemical reactivity

Deflagration is a heterogeneous process in which exothermic reaction occurs at a reaction front that moves at subsonic speeds through the unreacted material, propagating by heat conduction. Deflagration velocities vary from slow (1 to 10 mm min^{-1}) to fast (10 to 1000 m s^{-1}). Controlled deflagration occurs in solid rocket engines. In the heterogeneous process of *detonation*, exothermic reaction occurs at a reaction front that is a shock wave that moves at supersonic speeds through the unreacted material, propagating by heating due to extreme compression. Detonation velocities range from 1000 to 6000 m s^{-1}. Once detonation or energetic deflagration have been initiated, they proceed *relatively* independently of the surroundings. Although detonation and deflagration have many similarities, they are distinct processes: they propagate by different mechanisms and move in distinct velocity ranges. While both detonation and deflagration occur only in relatively energetic materials, the least energetic detonation requires considerably more energy than the least energetic deflagration. Nevertheless, an energetic deflagration may convert into a detonation, the *deflagration-to-detonation transition*.

Self-heating can occur in only moderately energetic reaction masses in the relatively adiabatic surroundings of plant-scale, unstirred vessels. If such self-heating cannot be brought under control and stopped, it is termed *runaway reaction*. More energetic reaction masses have produced self-heating even in stirred reaction vessels. Since the rate of heat evolution increases exponentially with temperature, while heat losses from the vessel to the surroundings increase only linearly, there is a temperature-of-no-return above which the self-heating cannot be brought under control and becomes a runaway. As the temperature continues to rise, further exothermic thermal degradation reactions possibly occur. The rates of increase of both temperature and pressure accelerate, the latter likely due to the production of volatile degradation products in addition to high vapor pressure at the high temperature. If the vessel is closed or its pressure relief system inadequate, the elevated pressure may exceed its mechanical strength, which is reduced somewhat by the high temperature, resulting in the abrupt failure of the vessel. This is *thermal explosion*. If the reaction mass is superheated when the pressure reaches ambient, part or all of the volatiles will flash to vapor. This is a BLEVE (Boiling Liquid Expanding Vapor Explosion). If the vapor is flammable and ignites, a fireball, flash fire or unconfined vapor cloud explosion results.

Fire is a diffusion-limited reaction between oxygen and a fuel that produces light, flame and heat. Although fire is a hazard due to chemical reaction, the evaluation of the fire hazard is generally considered to be a separate subject.

Laboratory Instruments

The most frequently used instruments are reaction calorimeters, differential scanning calorimeters, and adiabatic calorimeters. *Reaction calorimeters* are primarily used to carry out desired reactions exactly as they would be done at the plant scale, and simultaneously to determine reaction kinetics, enthalpies of reaction and/or solution, and the production of volatiles. These data are applied to optimize yield, to model kinetics, and to design plant equipment. The kinetics and enthalpies of reaction are valuable for identifying hazardous conditions such as an accumulation of unreacted reagents in a semi-batch reaction due either to a hangfire (a reaction that begins abruptly, after the passage of an induction period) or to too rapid addition (kinetics too slow to use up the reagent as fast as it is added at the given process temperature). *Differential Scanning Calorimetry* (DSC) is generally the most useful reactive hazards screening tool. In this technique a sample weighing anywhere from 1 mg up to 100 mg, depending on the instrument, is encapsulated in a high pressure cell and is heated at a constant rate (2–10°C min^{-1}) from ambient to 300–400°C. The instantaneous rate at which heat is generated or absorbed by the sample is measured continuously throughout the range scanned. The resulting DSC curve reveals all the thermogenic processes that occur in the temperature range scanned, and determines the total enthalpy of each process (by integration of peak area) and the temperature ranges over which the processes proceed at a significant rate. The isothermal mode of the DSC can then be used to determine the kinetics of individual processes, and, in particular, to check for induction periods due to autocatalytic decomposition or inhibitor depletion. The DSC can be used to determine the enthalpy and temperature range of the desired reaction, if this occurs sufficiently above room temperature, as well as all the undesired reactions, such as thermal degradations and polymerizations, that occur at higher temperatures. To fully realize the potential of DSC for reactive hazards screening, the instrument must be used with sample containers that can withstand pressures of 300–500 bar without leaking, and are composed of a material that does not react with or catalyze reaction in the sample. In addition, its linearity and calibration must be checked at high rates of exothermic heat generation, which are produced by highly energetic reactions. Finally, there are several commercially available adiabatic calorimeters that are essential for the further evaluation of a reactive hazard and for the design of pressure relief systems. Examples of such calorimeters are the *Accelerating Rate Calorimeter* (ARC) and the *Vent Sizing Package* (VSP2). The ARC sample bomb is a sphere about 2.5 cm in diameter composed of titanium, Hastelloy C or stainless steel. This bomb is suspended inside an adiabatic enclosure, a metal cylinder whose temperature is maintained equal to the sample temperature by a PID control loop. A heater is provided to raise the sample temperature in the absence of self-heating. In heat-wait-search mode, the sample temperature is raised to a programmed value, held until a steady-state is achieved and then held adiabatically for a programmed duration in an attempt to detect self-heating. The ARC can detect self-heating at rates as low as 0.02°C min^{-1}. If no self-heating is detected, the sample temperature is raised a programmed amount and the wait and search are repeated. If self-heating is detected, the sample is held adiabatically for hours or even days as the self-heating accelerates through the maximum rate of reaction to completion. In this way the kinetics of self-heating, the time to maximum rate of reaction and the total temperature rise are determined. However, as the heat capacity of the ARC sample bomb can be greater than that of the sample, a significant fraction of the heat released by the sample goes to heating the bomb rather than the sample. This slows self-heating and reduces the ultimate temperature increase considerably. To get the values for truely adiabatic self-heating, the experimental values must be corrected using the phi-factor, which is the ratio of the total heat capacity of the sample plus bomb system to the heat capacity of just the sample. Although a phi-factor equal to one is ideal, the ability to adjust the phi-factor by selection of bomb material and sample mass to values of about two or greater can be used to advantage. For example, one can separate exothermic processes that would overlap under ideal conditions, making it easier to determine and model the kinetics of each. The VSP2 sample cell is a cylinder, 120 mL in volume. It is constructed of thin sheet metal so that its mass is much less than the sample mass and the phi-factor of the sample plus cell system is nearly equal to one. The mechanical weakness of the VSP cell is compensated for by maintaining the pressure of its surroundings just below its internal pressure. Although the VSP2 cannot detect rates of self-heating as slow as the ARC can, the VSP2 simulates the course of a runaway reaction more accurately than the ARC. It is therefore used to determine directly the sizes of rupture disks or relief valves, as well as to validate mathematical models of runaway reaction, models whose parameters were possibly derived from ARC data. The VSP2 can also be operated with open cells to determine whether a reaction is tempered, and in blowdown experiments to characterize the composition and viscosity of the two-phase relief flow. The *Automatic Pressure Tracking Adiabatic Calorimeter* (APTAC) has been in use at Union Carbide since 1987 and has just come on the market. It is potentially an improvement to both the ARC and VSP2.

Hazardous chemical reactivity occurs at all scales

The thermal hazards evaluation of a substance or reaction mass takes place throughout the course of product development and into production. It generally begins when synthesis of the desired product is first carried out in kilogram quantities. It is wise to begin earlier – during the discovery phase, for example – if a material or reaction is thought to be energetic, as there is no point to investing good money in the development of a product that is too energetic to handle safely or in a manufacturing process that cannot be controlled safely. Of greater importance, of course, is that such energetic materials are hazardous to the chemist working at the bench.

At the *bench scale*, where synthetic chemists carry out reactions, distillations, etc., in glassware whose volume is 500 mL or less, the environment of the reaction mass is far from adiabatic, and exothermic reactions are usually easy to control. While runaways are infrequent, less is known about the hazards of the reaction mass in this early (possibly discovery) phase, so that detonations and deflagrations occur with some regularity. At *the prep lab* (*or kilo lab*) *scale*, operations are carried out in 20–30 L glassware. At the *pilot plant scale*, the chemical manufacturing process under development is scaled up to 200–500 L. At the *chemical manufacturing plant scale*, reactions are carried out in 20000–35000 L reactors and storage tanks are as large as 180000 L. As the scale of the reaction mass increases, the rate that heat can be removed (per kilogram of the reaction mass) decreases. Thus, the larger the reaction mass, the more adiabatic its environment and the more difficult reaction is to control. On the other hand, by the time a substance or reaction mass reaches plant scale, much more is known about its reactive hazards from the experience of synthetic organic chemists carrying out the reaction and as a result of the testing described below. As a result, the initial reactive hazards screening is concerned with identifying materials that can detonate, deflagrate rapidly, or runaway in glassware, while the latter stages are concerned with the identification of credible upset scenarios that result in runaway reaction at the plant scale, and with determining the worst of these. Reactive chemical hazards must also be identified to protect other operations such as drying and distillation, and for storage and transportation.

Strategy for the evaluation of reactive hazards

The following discussion is based upon the flow charts for a preliminary reactive hazards evaluation that are presented in the book *Guidelines for Chemical Reactivity Evaluation and Application to Process Design* [1, 2]. Also refer to books by Grewer [3] and Yoshida [4].

At the outset, an estimate of the hazard potential can be obtained from theoretical considerations. The presence of certain chemical structures [5] (such as nitro or nitramine groups) indicates a potential for detonation or deflagration. Enthalpies of reaction can be computed from enthalpies of formation, the latter being estimated by *ab initio* quantum mechanics [6, 7] or by Benson's method [8, 9] using the convenient NIST Structures and Properties Database [10] or using CHETAH [11]. The latter also computes two other valuable parameters: the oxygen balance and the maximum (exothermic) enthalpy of decomposition. These correlate well with explosibility. If the chemical species present are common ones, the literature could be searched [12–18] for reports of hazards. These theoretical methods alone cannot be relied upon to evaluate the reactive hazard. Screening tests **must** be performed.

DSC scans of raw materials, isolated intermediates, final products and then the intended process streams are the first screening tests done. These tests determine the temperature ranges and enthalpies of exothermic processes. An undesired exothermic reaction observed over a temperature range just above process temperatures indicates that loss of temperature control during the desired reaction could rapidly lead to a runaway, or, at least, to loss of product. Since the temperature range scanned by DSC is finite, further exothermic degradation likely occurs at temperatures above this range. The maximum enthalpy of decomposition, as computed by CHETAH, is used to estimate the magnitude of the heat released by the unobserved high temperature decomposition. If CHETAH calculates a maximum heat of about 1000 $J g^{-1}$ or more, a potential to deflagrate or detonate exists. A total heat as little as 200–300 $J g^{-1}$ (as seen by DSC) could lead to runaway reaction, depending on the environment. Additional screening tests, such as for pyrophoricity, reaction with process common contaminants such as water, catalysis by metals or metal oxides, etc., must also be done. The chemical manufacturing process must also be evaluated (with a HAZOP) for hazards due to the desired reactions, or process upsets, which many suggest further testing. If no hazards are detected in any of these screening tests, the hazards evaluation may be stopped.

If the maximum enthalpy of decomposition exceeds about 1000 $J g^{-1}$, the material may be capable of deflagration. Tests should be carried out for this and for sensitivity to impact, static discharge and friction. Note that deflagration tests of relatively less energetic materials are sensitive to the degree to which the sample has been compacted, and to whether the sample is completely surrounded by a container or not. If the maximum enthalpy of decomposition exceeds 3000 J g^{-1}, the sample may detonate. In addition to the tests for deflagration and sensitivity to impact, etc., tests should be run to determine speed of propagation (BAM 50/60 or TNO 50/70 steel tube tests) and explosive power (e.g., lead block or ballistic mortar tests). Such tests are sensitive to the quantity, density, temperature, and diameter of the sample, as well as to the presence of bubbles or cavities, the size and polymorphic modification of crystals and the rigidity of confinement. If a sample does detonate or deflagrate, precautions must be taken, or it may be considered too hazardous to make, store or ship in bulk.

For samples that generate more than 200–300 J g^{-1}, but do not deflagrate or detonate, the potential for runaway reaction must be evaluated. The plant can then possibly be designed to prevent the runaway. A pressure relief system for the reactor or storage vessel to mitigate the worst credible runaway scenario, or at least the fire load, must also be designed. The DSC curve gives an indication of the range over which undesired reaction proceeds at a rate fast enough for the DSC to detect. However, self-heating under near-adiabatic conditions in plant scale equipment can occur at temperatures well below this range. Therefore, samples are run in the ARC to determine the kinetics of self-heating at the lower temperatures. In addition, ARC runs measure the rate of pressure increase, and so determine temperatures where the production of volatiles by thermal degradation occurs. ARC data are routinely used to model the kinetics of undesired reactions [19]. If the temperature range where self-heating due to undesired reaction (as detected by the ARC) overlaps the highest temperatures the intended reaction could achieve under credible upset conditions, runaway reaction could proceed to very high temperatures and pressures. HAZOP scenarios in which upset conditions (mischarging, reverse additions, contamination, loss of agitation, etc.) lead to a runaway starting at process temperatures must be exhaustively evaluated. Simulations of these scenarios in the VSP2 are done to determine the worst credible scenario – the one where the maximum rates of increase of pressure and temperature are highest. The case where an external fire load drives a reaction mass to runaway might be a worst credible scenario, for example. The worst credible scenario then serves as the design basis for the emergency relief system (ERS). The ERS must be designed to halt the rise in temperature and pressure well before the containment vessel is 20% above its maximum allowed working pressure, to prevent a thermal explosion. This design task is usually difficult because the relief flow out of reactors is likely to be choked and consist of a two-phase (vapor/liquid) fluid in which reaction is possibly ongoing and liquid is flashing into vapor. Methodology for ERS design for such relief flows was produced through the DIERS project [20–22]. The sizes of vents or relief valves are obtained from Leung's ω–method [23] using the VSSP or VSSPH [24] programs and VSP2 data, or from programs such as SAFIRE [25] or SuperChems [26], which require the input of kinetic models and physical property data.

References

1 Center for Chemical Process Safety, Guidelines for Chemical Reactivity Evaluation and Application to Process Design, American Institute of Chemical Engineers, New York 1995.
2 A. S. West, Process Safety Progress, 12 (1993) 55.
3 T. Grewer, Thermal Hazards of Chemical Reactions (Industrial Safety Series: Vol. 4), Elsevier, Amsterdam 1994.
4 T. Yoshida, Safety of Reactive Chemicals (Industrial Safety Series: Vol. 1), Elsevier, Amsterdam 1987.
5 Bretherick's Handbook of Reactive Chemical Hazards (5th Ed.), P. G. Urben (Ed.), Butterworth-Heinemann, Oxford 1996, Structures Relevant to Explosibility.
6 M. J. Frisch, A. Frisch and J. B. Foresman, Gaussian 94 User's Reference, Gaussian, Inc., Pittsburgh 1994, p. 72.
7 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, J. Chem. Phys., 94 (1991) 7221.
8 S. W. Benson and J. H. Buss, J. Chem. Phys., 29 (1958) 546.
9 S. W. Benson et al., Chemical Reviews, 69 (1969) 279.
10 S. E. Stein, NIST Standard Reference Database 25, NIST Structures and Properties Database and Estimation Program, National Institute of Standards and Technology, Gaithersburg 1994.
11 NIST Special Database 16, The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation, CHETAH 7.0, National Institute of Standards and Technology, Gaithersburg 1994.
12 R. J. Lewis, Sax's Dangerous Properties of Industrial Materials (8th Ed.), Van Nostrand Reinhold, New York 1992.
13 F. Lees, Loss Prevention in the Process Industries (2nd Ed.), Butterworth-Heinemann, Oxford 1996.
14 Manual of Hazardous Chemical Reactions (5th Ed.), National Fire Protection Association, Boston 1975.
15 Chemical and Engineering News Safety Notes Index 1976-1989, American Chemical Society, Washington, D. C., 1991.
16 Chemical and Engineering News Online (Safety Notes), CEN, STN International, Chemical Abstracts Service, Columbus.
17 CHEMSAFE, STN International, Chemical Abstracts Service, Columbus.
18 Chemical Safety NewsBase, CSNB, STN International, Chemical Abstracts Service, Columbus.
19 See, for example, M. Ahmed, D. D. Goetz, H. G. Fisher and A. M. Janeshek, International Symposium on Runaway Reactions and Pressure Relief Design, G. A. Melhem and H. G. Fisher (Eds), American Institute of Chemical Engineers Publications, New York 1995, p. 283.
20 H. G. Fisher et al., Emergency Relief System Design Using DIERS Technology, The DIERS Project Manual, American Institute of Chemical Engineers Publications, New York 1992.
21 H. G. Fisher, Plant/Operations Progress, 10 (1991) 1.
22 H. G. Fisher, Process Safety Progress, 14 (1995) 87.
23 J. C. Leung, International Symposium on Runaway Reactions and Pressure Relief Design, G. A. Melhem and H. G. Fisher (Eds), American Institute of Chemical Engineers, New York 1995, p. 200.
24 J. C. Leung, VSSPH User's Manual, Fauske and Associates, Inc., Burr Ridge, IL, 1994.
25 SAFIRE, Systems Analysis for Integrated Relief Analysis, (Publication B-1, Version 10. 0), American Institute of Chemical Engineers Publications, New York.
26 SuperChems for DIERS (Publication B-5, 2nd Ed.), American Institute of Chemical Engineers Publications, New York 1996.