Case History 08 : « Amination »

Author Francis Stoessel

What happened

After 40 years of accident-free production of nitroaniline, an explosion occurred with severe consequences for the building and its surroundings. A part of the autoclave weighing 6 tonnes was catapulted 70 meters.
Subsequent enquiries revealed the following:

1. The batch causing the accident had a massive overcharge of chloronitrobenzene and through that an undercharge of ammonia. This raised the reaction energy of the starting material mass, and lowered the reaction speed and pressure below those specified.
2. Kinetic studies of the defective batch showed that the jacket cooling was capable of dissipating the amination heat up to approx 190°C.
3. Due to an impact at one end of the scale, the temperature registration (0-200°C) inaccurately indicated 194°C.
4. The autoclave was equipped with a separate pressure venting pipe, a safety diaphragm, and a blow-off valve connected to it in series (pick-up pressure 50 bar in each case). It was clear from the debris that these mechanisms had been activated.
5. Thermal balance calculations show that the reactor could have been relieved via gas flow through the safety diaphragm/valve up to 250°C/65 bar. When the accident happened, the mass was not capable of being relieved even at lower temperatures, because a liquid/ gas flow had occurred.
6. It must be assumed that pressure had built up between the safety diaphragm and the safety valve due to faulty seals (ie in the worst case the actual pick-up pressure could have amounted to 2 x 50 = 100 bar).
7. It may be concluded from thermic studies that the heat release due to decomposition attributed to the nitro group made a substantial contribution to the destructive power of the thermic explosion from 350-400°C.
8. Reconstructed temperature/time profile (See Figure on next page)

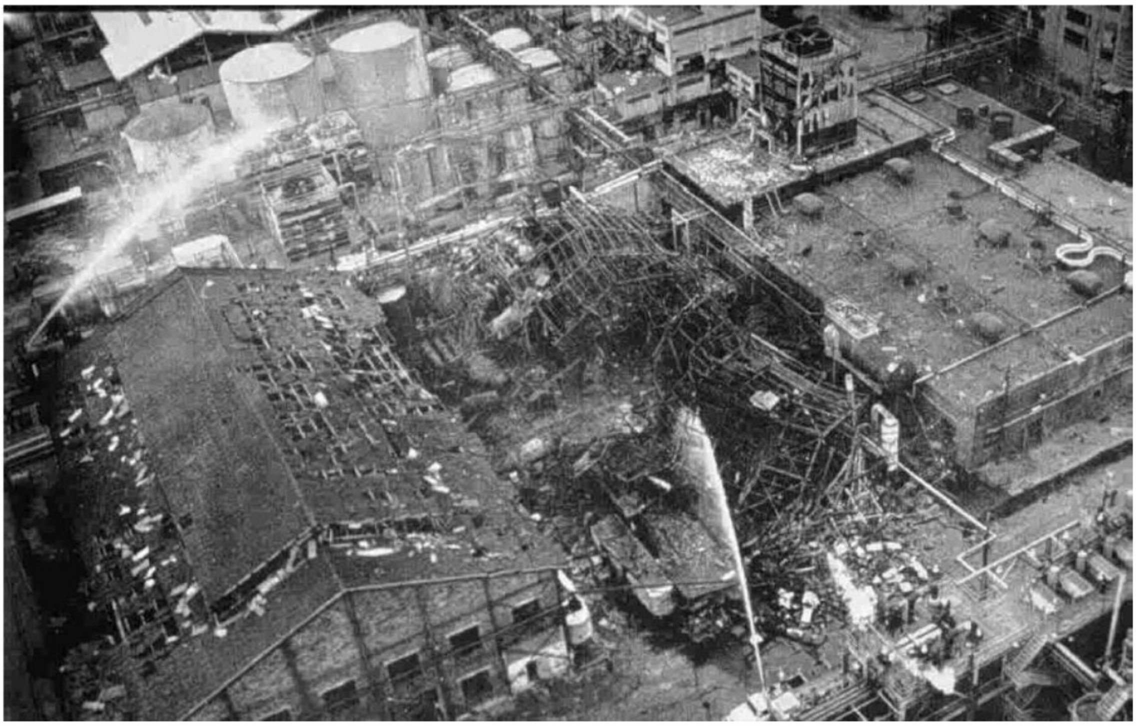


Figure 1 : **Explosion Monsanto Sauget Illinois 1969**

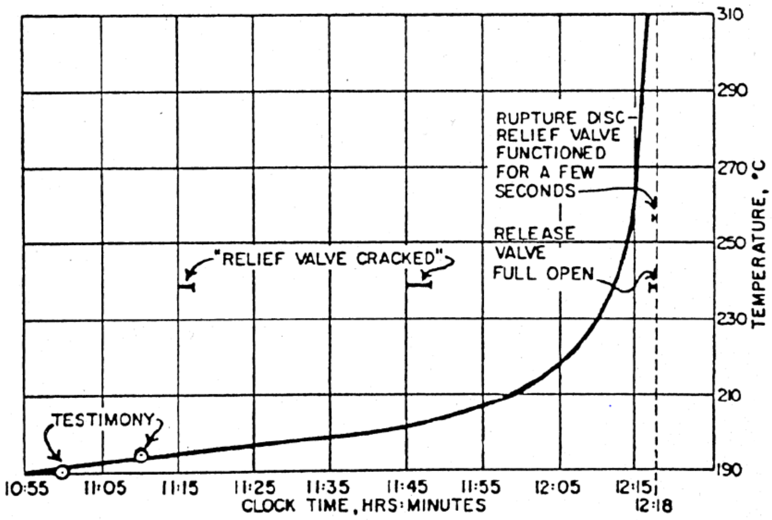


Figure 2 : **Reconstructed temperature course**

Source: G.C. Vincent, "Rupture of a Nitroaniline Reactor" Loss Prevention, AICHE, New York, Vol 5 (1971)

SACHE Case Histories and Training Modules

Ronald J. Willey
Department of Chemical Engineering, 342 SN, Northeastern University, Boston, MA 02115

Training can be simplified. Vivid slides of case histories of accidents, supplemented with easy-to-use lecture notes for the universities and industry, are now available through AIChE's Center for Chemical Process Safety (CCPS). Since 1991, a committee composed of approximately seven academics, seven industrial representatives, and three government representatives have worked together to produce teaching modules for use in the undergraduate educational experiences at colleges and universities. This committee, called the Undergraduate Education Committee (UEC), was established by CCPS to enhance chemical engineering undergraduate education in the area of chemical process safety. To date, the committee has produced 6 problem sets, and 15 case histories/training modules that consist of slides and lecture notes. These products are made available to universities who join a group called SACHE (Safety and Chemical Engineering Education) and can be used by instructors in classroom and seminar formats. The focus for this paper is a summary of case histories available (Tank Failures, Nitroaniline Reactor Rupture, Seveso, Bhopal, and Pasadena). Industry can also benefit by using these informative modules in training their technical employees

INTRODUCTION

The American Institute of Chemical Engineers (AIChE) has a history of involvement in process safety and loss prevention for chemical and petrochemical plants. In 1985, the Center for Chemical Process Safety (CCPS) was established to intensify the development and dissemination of the latest scientific engineering practices for the prevention of catastrophic incidents involving hazardous materials; to advance the state-of-the-art engineering practices through research; and to develop and encourage the use of undergraduate engineering curricula that will improve the safety knowledge and consciousness of engineers. To meet the third objective, CCPS formed the undergraduate education committee (UEC) in 1989.

After formation of the committee, a requisite assessment was done. The UEC decided that teaching aids were needed for professors. The first product produced by this group was a tutorial set of 90 problems that were sold at modest costs to chemical engineering departments [1]. The problems were designed in a way that chemical process safety was incorporated into fundamental chemical engineering courses. Problems were developed around chemical engineering topics such as material balances, energy balances, momentum transport, kinetics, thermodynamics, heat transfer, and mass transfer.

Presently, the membership of the UEC constitutes seven professors from the faculty of various U.S. chemical engineering departments, seven chemical engineers from industry, three retired engineers from industry, and one representative from government. The committee meets three times a year. The major activities of the UEC include project development, project review, and overseeing annual workshops in chemical process safety for chemical engineering faculty. In 1996 and 1997, the workshop was held at BASF in Wyandotte, MI. The 1998 and 1999 workshops took place at The Dow Chemical site in Freeport, Texas. The committee approves 7 to 10 projects per year for distribution as teaching aides to chemical engineering departments around the United States and Canada. Presently, 100 universities have joined SACHE at an annual fee of $300. In addition, a significant subsidy is provided to SACHE from CCPS. These funds cover expenses incurred in developing teaching aids for chemical process safety.

A Generic Description of a Case Study and the Review Process

Most case studies originate from committee suggestions based on accidents that have come to the attention of a particular member. Occasionally, committee members have personal connections through direct experience to the case study. Other case histories have evolved from interviews with national and international experts within the field. For example, the "Seminar on Tank Failures" is based on personal visits to several national experts in the general area of storage tanks. A case history goes through extensive committee review and, once accepted, copies are produced and distributed through CCPS.

In general, a case history attempts to set the stage before the defining event. Background is provided outlining the local history of the community and company as relevant to the case. The normal operation conditions are discussed. Because case studies are targeted to undergraduate chemical engineering students, a review of chemical engineering fundamentals

e-mail: willey@neu.edu

TABLE 1. SACHE Case Studies Available from AIChE-CCPS

Title	Author	Year	ISBN Number
Seminar on Tank Failures - Slides and Lecture	Willey	1993	ISBN 0-8169-0602-5
Fires - Slides and Lecture	Welker/Springer	1993	ISBN 0-8169-0603-3
Explosion Proof Electrics - Slides and Lecture	Cyanamid/Page	1993	ISBN 0-8169-0599-1
Process Safety Management with Case Studies: Flixborough and Pasadena (TX) and Other Incidents - Slides and Lecture	Bethea	1994	ISBN 0-8169-0608-4
Seminar on Nitroaniline Reactor Rupture - Slides and Lecture	Willey	1994	ISBN 0-8169-0634-3
Seminar on Seveso Release Accident Case History - Slides and Lecture	Willey	1994	ISBN 0-8169-0634-4
Dust Explosion Control Video/Slide/Lecture	Louvar/Schoeff	1994	ISBN 0-8169-0634-4
Toxicology and the Chemical Engineer - Slides and Lecture	Welker/Springer	1995	ISBN 0-8169-0606-8
Consequences of Operating Decisions-Lecture	Cobb	1995	ISBN 0-8169-0633-5
Industrial Hygiene and the Chemical Engineer - Slide Lecture	Springer/Welker	1995	ISBN 0-8169-0604-1
Phillips' Explosion -Video	Bethea	1996	ISBN 0-8169-0673-4
Inherently Safer Plants - Slides and Lecture	Kubias	1996	ISBN 0-8169-0669-6
Property of Materials - Slides and Lecture	Willey	1997	ISBN 0-8169-0694-5
The Bhopal Disaster - Video/Slide/Lecture	Willey	1998	ISBN 0-8169-0766-8
Potential Accidents from Safety Systems - Slide and Lecture	Hendershot	1998	ISBN 0-8169-0732-3
Emergency Response Planning - Slide and Lecture	Bethea	1998	ISBN 0-8169-0671-8
The Human Healthrisk Assessment Process - Slide and Lecture	Jayjock	1998	ISBN 0-8169-0734-X

relevant to the case is offered. Ideally, the instructor relates the case study to chemical engineering courses that students have taken. Next, a detailed description of the defining event is given. Afterward, the root causes and/or lessons learned are presented to enable the student estimate how to avoid similar mistakes. Slides from photographs taken at the actual event as well as word slides are used to explain the situation to the student. A few case studies come with videotapes related to the event. Table 1 is a listing of case histories prepared for SACHE.

Property of Materials

Property of materials, although not a case history, is a simplified training mechanism that can be used with entry-level employees. This slide lecture is developed around the items presented in material safety data sheets (MSDS). A strong focus is placed upon physical properties such as boiling point, specific gravity, flammability terms (LFL, UFL), and reactivity. The impacts of particle size, viscosity, and thermal deformation as related to inhalation exposure, heat transfer, and mechanical failures respectively are discussed. Shown in Figure 1 is one of the slides from this package which is the flammability diagram for methane-oxygen and nitrogen mixtures. This package is an excellent package for new employees and technicians to review.

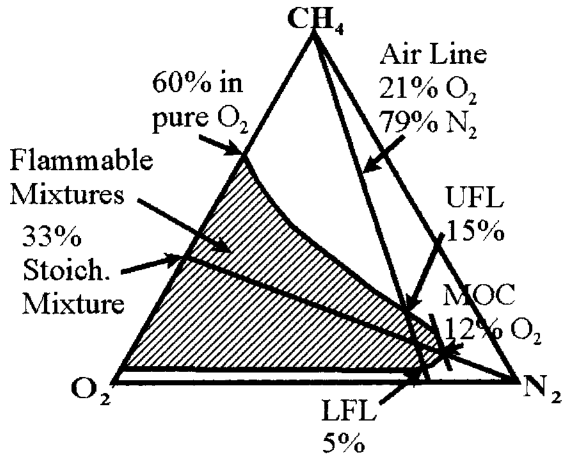


FIGURE 1. Methane flammability diagram. From "Properties of Materials," Willey 1997.

Seminar on Tank Failures (Willey, 1993)

The slide package "Seminar on Tank Failures "contains three detailed case histories: BLEVEs (boiling liquid expanding vapor explosions) that occurred in Mexico City in 1984, a failure of a natural gas storage tank in 1944, and a failure of a diesel storage tank in 1988. Figures 2 through 4 are taken from this case history. Figure 2 shows the erection of a storage tank. This figure demonstrates how many case histories include background information. In this example the concept examined is "what is a tank and what are the various types of storage tanks?". The case history about BLEVEs is from material supplied by the Skandia group of Stockholm, Sweden. The event at Mexico City was one of the worst ever in terms of fatalities as more than

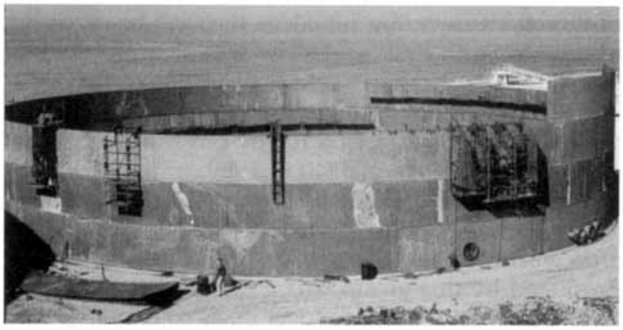


FIGURE 2. Field construction of a large storage tank. From "Seminar on Tank Failures," Willey 1993.

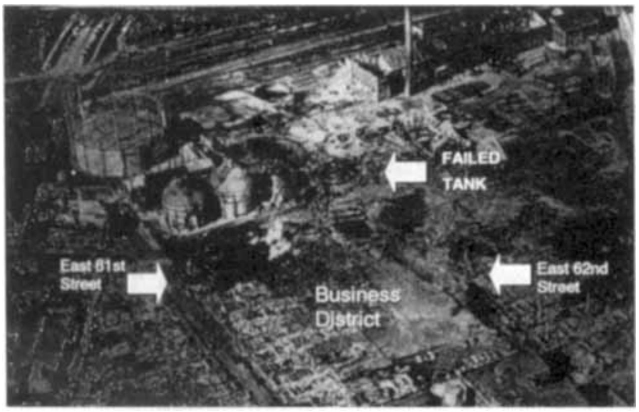


FIGURE 3. Aerial shot of Cleveland streets after 1944 LNG tank failure and subsequent explosion. From "Seminar on Tank Failures," Willey 1993 (adapted from Bureau of Mines Report of Investigations, #3867, 1945).

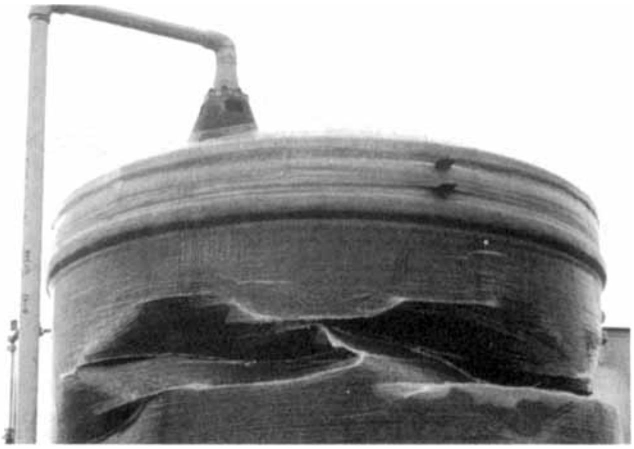


FIGURE 4. Sucked in acid storage tank from "Seminar on Tank Failures." Willey 1993 Photo courtesy of Roy Sanders.

500 people were killed when 15-20 ton storage tanks at a liquid petroleum gas (LPG) facility BLEVEd. This case explains the steps that are involved in a BLEVE and it goes on to discuss how to prevent BLEVEs from occurring. If LPG is used in a facility, this is a good case history to employ when introducing employees to the precautions required for handling LPG.

The next case history in "Tank Failures" focuses on a liquefied natural gas (LNG) tank failure. An LNG storage tank is really a tank within a tank. It is similar to a large thermos bottle. The inner tank holds LNG at slightly above atmospheric pressure. Thus, the storage temperature is -162°C (-260°F). The outer tank holds insulation in place. The inner wall for an LNG storage tank erected in Cleveland in the early 1940's was composed of 3% Ni steel. It was learned the hard way that this steel can suffer brittle failure at the low storage temperatures of LNG. More than 1,500 people were left homeless, and approximately 120 people died as a result of this tank failure. When the tank failed, liquid methane did not immediately vaporize. Instead the liquid flowed into the sewers along the city streets. Eventually, the liquid methane vaporized along the sewers and an ignition source was found. The resulting explosion blew up four city blocks (see Figure 3). The lesson learned here is related to material specification. Over time, engineers learned that wall material for LNG tanks need to be 9% nickel steel. The impact of this explosion on the public perception of methane storage was such that it took almost 20 years before another LNG tank was installed in the United States.

The third case history in "Tank Failures" explores a failure of a diesel oil storage tank. The story begins with a tank relocation from Cleveland to Pennsylvania. Several unsafe practices were involved. These included cutting the old tank above wells, failing to get proper permits, deciding to neglect the negative results of compaction tests, ignoring radiographs that showed defective old welds, and omitting a full hydrostatic test. The tank failed because of brittle failure possibly initiated at a defective old weld when the combination of a very cold January day and a filled tank coincided. A major lesson to be learned from this case history is the necessity to follow standards and recommendations that were laid down by regulatory and professional associations.

"Tank Failures" concludes with a review of the more common tank failures as shown in Figure 4. The acid storage tank displayed in Figure 4 was sucked in. While the tank was being filled with sulfuric acid the tank overflowed through an overflow line. The alert truck driver immediately closed the delivery valve. Nonetheless, a syphon action had been created by the overflow and the tank was sucked in and destroyed [2] .This portion of the case history is of value when training new personnel who are unaware of the fragile nature of storage tanks.

The Bhopal Disaster (Willey, 1999)

The slide package "The Bhopal Disaster" is the latest SACHE case history. It includes slides and text developed from more than 100 sources on the disaster. Also included is a copy of one of the definitive papers presented on the case by Ashok S Kalelkar, of Arthur D. Little Inc., [3].and a video entitled "Unraveling the Tragedy at Bhopal."

Late December 2, and early December 3, 1984, slightly more than 500 kg of water entered into a storage tank containing 41 metric tons of methyl isocyanate (MIC) at a pesticide plant located in Bhopal, India, partially owned by Union Carbide Corporation. This entry of water initiated a number of exothermic reactions. These reactions caused the temperature and pressure of the storage tank to rise. At approximately 12:45 a.m. on December 3, the pressure inside the tank exceeded the pressure setting on the relief valve. The release followed the relief valve vent header (RVVH) to a vent gas scrubber (VGS) system and flare stack. Regrettably, both of these safety control systems were not operational. Consequently, the release from the relief valve entered the environment and followed the prevailing winds which carried the extreme toxin, MIC, into the slums and shanty towns that surrounded the plant resulting in more than 2,000 fatalities. More than 200,000 people were exposed to the toxic emissions. Of this group, it is estimated that 50,000 people suffer long-term effects from the exposure to-date.

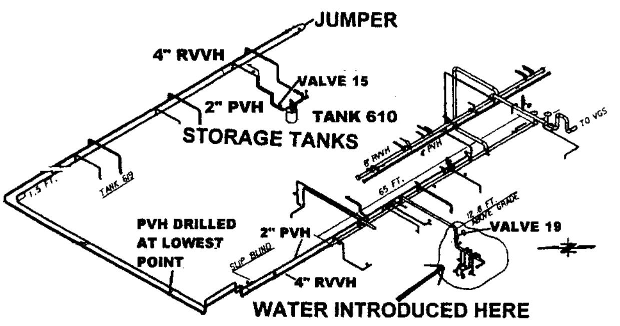


FIGURE 5. Relation of relief valve vent header and process vent header to MIC storage tank and point of wash water entry from "The Bhopal Disaster," Willey 1998, (adapted from Kalakar [3].

The case history gives a detailed examination regarding how water entered into the MIC storage tank. Two major explanations have evolved: the water washing theory and the deliberate admission of water directly into the tank. In the water washing theory (illustrated in Figure 5) water was introduced into a pressure filtering area for the purpose of unclogging some plug lines. Normally, these filters are isolated from the RVVH by using a slip blind. On that fateful day, the blind was not installed. Although exact details are unclear, essentially water flowed from the filters into the RVVH and followed a 4" RVVH line around a jumper down to a 2" process vent header (PVH) through a control valve (Valve 15 in Figure 6) into one of the three MIC storage tanks.

The other explanation is based on the testimony of a plant employee; the hydraulics required to fill the RVVH and PVH lines; indications that Valve 19 (Located between the filters and the RVVH line in Figure 5) was closed during the washing, and evidence that no water was found when the Indian Central Bureau of Investigation drilled a hole in the lowest point on the process vent line. An employee at the plant testified

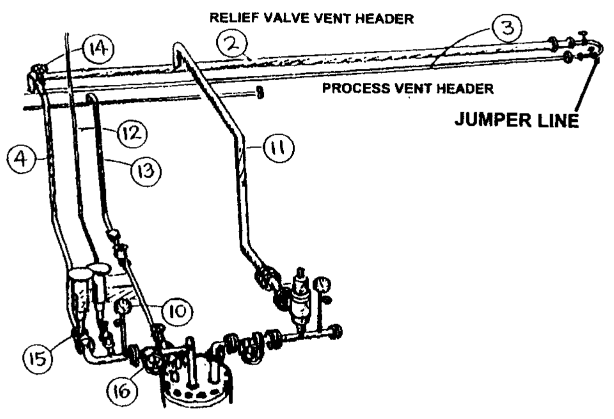


FIGURE 6. Schematic of RVVH and PVH connections at top of MIC storage tank from "The Bhopal Disaster," Willey 1998, (adapted from Kalakar [3]).

that a pressure gauge (Gauge 10 in Figure 6) was missing on the morning after the accident. It has been alleged by a Union Carbide lead team that an employee on the third shift committed sabotage.

The lessons learned from this tragedy are many. First, companies should have contingency plans available for dealing with major accidents. They must include the public in their risk management programs under the "Right to Know" laws, and through Community Action Emergency Response (CAER) programs. The consequences of suspending safety systems must be fully understood by management. In addition, efforts should be made to reduce inventory of hazardous chemicals. A quote from Trevor Kletz best summarizes this lesson: "What you don't have, can't leak, catch on fire, or cause any other problems" [5]. Finally, whenever possible, look for alternative routes in which the chemistry involves less hazardous intermediates.

Review of this case history by technical employees will demonstrate how fragile a company's relationships with communities can be. It demonstrates the consequences of poor decision-making, especially, when safety systems are taken out of service.

Seminar on Seveso Release Accident Case History (Willey, 1994)

The Seveso, Italy, accident involved the release of TCDD 2,3,7,8 tetrachlorodibenzo-dioxin or simply dioxin on July 10, 1976, from a chemical plant located just north of Seveso in the town of Meda. The dioxin formed when two molecules of the sodium tri-chloro phenol combined. This occurred when a batch reactor used for the formation of tri-chlorophenol was left over a weekend at a state of partial completion (it has been alleged that the crew didn't finish the batch as instructions directed). The batch was left at the processing temperature and no quench water was added. Self heating began. Seven hours later the reactor pressure exceeded the relief system and a runaway had occurred. In this particular case, the relief system worked. The exit of the relief system, however, was piped directly into the environment above the plant. The release, which contained about 2 kg of dioxin, moved in the wind direction toward populated areas east and southeast of Seveso centers. Initially, the effects of the release were not observed. Gradually, however, over a two-week period much of the wildlife in the affected zones died and children began to display symptoms of chloral acne. Eventually, medical experts deduced that dioxin poisoning had occurred. Hundreds of families were relocated as results of the contamination by dioxin. It is only recently, 20 years later, that the worst areas of contamination were opened to the public.This case study demonstrates several chemical process safety concepts of interest to chemical process plant operating and technical personnel. It discusses the toxicity of materials especially dioxin which is an extreme toxin. It reviews runaway reactions. It discusses the consequences of operating decisions which differ from written procedures. In addition, the case history demonstrates dispersion patterns that can result when a release of highly toxic chemicals reaches the environment.

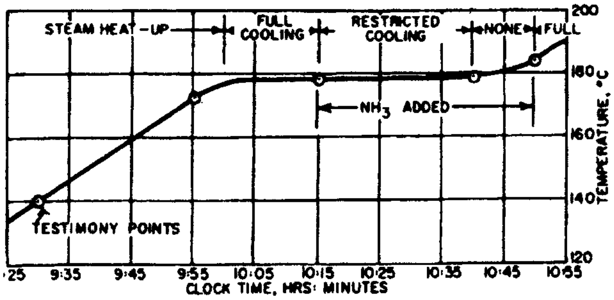


FIGURE 7. Temperature-time data in the early stages of a nitroaniline reactor runaway. From "Seminar on a Nitroaniline Reactor Rupture," Willey 1994 and originally appeared in Vincent [6] Figure 11.

Seminar on a Nitroaniline Reactor Rupture (Willey, 1994)

The slide package "Seminar on a Nitroaniline Reactor Rupture" deals with a case history that was presented in 1971 by Vincent [6]. This case history is an example of an accident that occurred before management of change guidelines appeared in OSHA [7].A pump in the plant needed to be repaired. This pump was used for the transfer of ortho nitrochlorobenzene into an autoclave. A decision was made to override the safety systems during the pump repair. Essentially, the operators were told to be careful when filling the autoclave. Under normal circumstances, the reactor was filled with excess (7.5 times the stoichiometric amount) 26 Be NH_3 solution. Thus, the reactor kinetics was pseudo first order in the concentration of ortho nitrochlorobenzene (ONCB).This time, however, more than two times the normal amount of ONCB was added to the reactor. Further, the ammonia solution added was weaker than normal. Initially, the reactor did not come up to the expected pressure when the normal operating temperature was reached (the temperature-time data are shown in Figure 7). Consequently, the operators restricted cooling and began to add more ammonia solution. Within a few more minutes the operators began to recognize that something was even more abnormal with this batch. Temperature unexpectedly rose above the normal operating temperature. Full cooling was recommenced. Temperature continued to rise. This was because the intrinsic rate of reaction was 2.18 times higher than normal. Consequently, the heating rate (this was an exothermic reaction) per unit volume was 2.18 times higher than normal and eventually the heating rate exceeded the heat removal rate by the cooling system - a runaway reaction.

The characteristics of this runaway were as follows: initially the reactor temperature rose only 6°C over the first 30 minutes; however, during the next 30 minutes the temperature rose 20°C. In the next five minutes, the temperature rose another 20°C and in the final two minutes temperature rose 50°C. Figure 8 shows the estimated temperature, pressure, and conversion profiles. Note how things rapidly change in the last 15 minutes between 12 and 12:15 a.m. This is an example of a runaway reaction. The point of no return, heat generated by the exothermic reaction exceeding

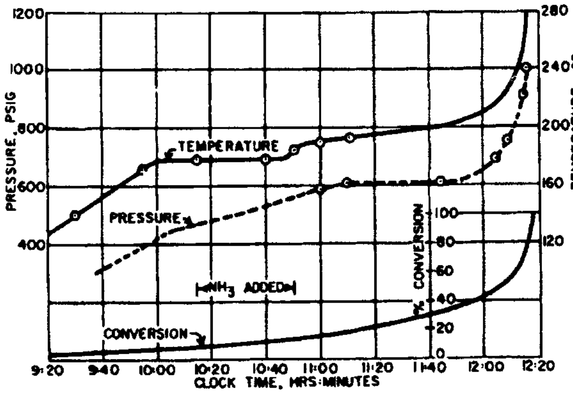


FIGURE 8. Temperature-time data in the early stages of a nitroaniline reactor runaway. From "Seminar on a Nitroaniline Reactor Rupture." Willey 1994 and originally appeared in Vincent [6]. Figure 13.

the rate of heat removal, was 188°C. Two exothermic reactions were involved. The first was the exothermic reaction of ONCB and ammonia to nitroaniline. The second was the exothermic reaction created by the decomposition products of nitroaniline and ammonium chloride. The resulting over pressure of 1400 psi created an explosion that was heard eight miles away. Fortunately, no one was killed.

The lessons learned include the need for redundant backup. In this case, the reactor temperature was measured by a chart recorder. This temperature display stuck at 194°C while the reading of its maximum temperature was 200°C. Thus, the operators were unable to monitor temperature beyond 194°C. Another issue discovered from the examination of this accident was the requirement of having a telltale pressure gauge between the relief valve and the rupture disk (Figure 9). The release system had been designed to relieve the reactor when pressures exceeded 695 psi. If the relief system had gone off at this pressure, no explosion would have occurred. In this case, the rupture disk had developed a small pin hole and thus, created a compound pressure relief system which required a total ΔP of almost 1400 psi before opening. This case history exemplifies the need for management of change guidelines.

Explosion at the Phillips 66 Company (Pasadena) Houston Chemical Complex (Bethea 1994,1996)

Dr. Robert Bethea has written two SACHE products about the accident at the Phillips 66 Company's Houston Chemical Complex (HCC) in Pasadena, Texas that occurred on October 23, 1989. The first product "Process Safety Management with Case Studies: Flixborough, Pasadena (TX), and Other Incidents," examines process safety management (PSM) reviews, process safety management of hazardous chemicals, the Flixiborough disaster, and the Pasadena, TX disaster. The portion about Pasadena is based around the Report to the President and the intense scrutiny of various governmental agencies such as the Occupational Safety and Health Administration. Also included in this package are six mini case studies that demon-

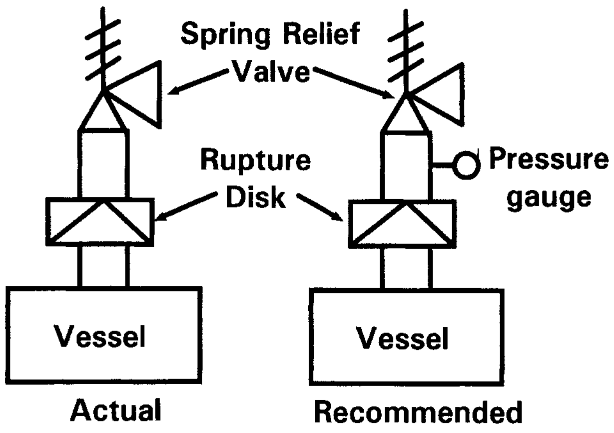


FIGURE 9. Comparison of relief system piping used for a nitroaniline reactor compared to recommended practice. From "Seminar on a Nitroaniline Reactor Rupture," Willey 1994.

strate various aspects of chemical process safety. The second product related to Pasadena is a videotape which is composed of edited news footage taken during the disaster. The video contains eyewitness accounts, statements by Phillips 66 employees and representatives, and actual newsreel footage. The video is divided into five sections: one on the day of the explosion, and one for each of the following four days. The story of the explosion and subsequent events such as fire fighting, search and rescue, and cleanup are described as they have unfolded. In addition, the effectiveness of the Phillips emergency response plan and two of its deficiencies are highlighted as is formation and effectiveness of the Channel Industries Mutual Aid Association. Technical personnel that watch this video and review this case history will gain a sense of how information about an accident evolves and becomes reported by the media.

Case Histories in Development

The UEC continues searching for new case studies that can be used in teaching environments. Presently, ten are planned over the next three years. These include chemical/petrochemical plant explosions at Seadrift, TX; Montreal Canada; Milford Haven, Wales; and a distillation column accident. New teaching modules are also in development about designs for over pressure and runaway reactor protection, pump cavitation, corrosion, and advanced emergency shutdown. The SACHE committee is always open to new suggestions and product developers. Interested persons should contact Mr. Owen Kubias, CCPS-AICHE, or the author.

CONCLUSIONS

The need to incorporate chemical process safety into the classroom has always existed. Those over the age of 50 can recall a professor or two who cited concerns about safety and safe behaviors because these professors often had industrial experience. In more recent times, however, many professors do not have industrial experience to call upon. Furthermore, their emphasis, promotion, and evaluations are based around research. The primary focus of the UEC is to offer teaching aides that promote chemical process safety. Further, these aides should be of interest to the industrial community as well as a means to achieve efficient training and provide a reminder as to why matters have evolved the way they have (management of change requirements for example).

ACKNOWLEDGMENT

The author acknowledges the entire SACHE committee for their many hours of review and suggestions in the preparation of these various case histories. Dr. Walt Howard is especially noted for his many insights during these review sessions.

LITERATURE CITED

1. **Welker, J.R. and C. Springer,** "Safety, Health, and Loss Prevention in Chemical Processes: Problems for Undergraduate Engineering Curricula, CCPS-AIChE, New York (1990).
2. **Sanders, R.E.,** "Management of Change in Chemical Plants: Learning from Case Histories," Butterworth Heinemann, Oxford, UK (1993).
3. **Kalelkar, A.S.,** "Investigation of Large-Magnitude Incidents: Bhopal as a Case Study," in IChemE Symposium Series No. 110,The Institution of Chemical Engineers, U.K. pp 553-575 (1988).
4. **Sutcliffe, V.,** *Occupational Hazards,* pp.65 (July, 1998).
5. **Kletz, Trevor,** "Lessons Learned from Disaster," The Institution of Chemical Engineers, U.K. p. 8 (1993).
6. **Vincent, G.C.,** *Loss Prevention,* Vol. 5, AIChE, New York (1971).
7. **Occupational Safety and Hazard Administration (OSHA)** 1910.119 "Compliance Guidelines and Recommendations for Process Safety Management".
8. **Elliot, M.A., C.W. Seibel, F.W. Brown, R.T. Artz and L.B. Berger,** "Report on the Investigation of the Fire and Liquefaction, Storage, and Regasification Plant of the East Ohio Gas Company, Cleveland, Ohio, October 20, 1944," U.S. Bureau of Mines, RI 3867, Pittsburgh, PA (1945).

This paper (28b) was presented at the AIChE 33rd Annual Loss Prevention Symposium in Houston, TX March 17, 1999.

Thermo-Kinetic Analysis of Reactions Involved in the Manufacture of o-Nitroaniline

Ronald J. Willey,[a] Fausto Rodrigues,[b] Simon Chippett,[b] Georges Melhem,[b] and Surendra K. Singh[b]

[a] Department of Chemical Engineering, Northeastern University, Boston, MA 02115

[b] Arthur D. Little, Inc., Cambridge, MA

Exothermic reaction processing must be concerned with potential consequences when heat released by the reaction exceeds that removed by the reactor coolant system, a situation known commonly as a runaway reaction. We have investigated a complicated reaction process in which two exotherms can occur—the process of making the desired product, o-nitroaniline (o-NA), from ammonia and o-chloronitrobenzene (T Onset around 140° C), and the decomposition of the product, o-NA (T Onset around 225° C). A severe industrial loss occurred in 1971 at a plant producing o-nitroaniline, an incident that has been the subject of several AIChE loss prevention presentations and papers. In this article, we take a closer look at the chemistry involved, and the ability to use thermo-kinetic analyses to understand the reactions involved, and how these influenced the accident that occurred. Further, we present the progress we've made towards predictive models for the kinetics and the pressure-time data. Several useful generalizations have evolved. First, is the need to include experiments that use stoichiometric mixtures when assessing exothermic reactions. Second, is the need to understand the role of reaction intermediates, and how they may influence the operation of the plant.

INTRODUCTION

The Main Reaction and the Original Accident Background

The chemistry and process behind the 1971 incident mentioned in the abstract is described in detail in Groggins [1]. Essentially, two ingredients are used: aqueous NH_3 solution 26° Be (28 to 30% NH_3 by wt %) and o-chloronitrobenzene.

o-CNB ($C_6H_4ClNO_2$) + 2 NH_3 $\rightarrow$ o-nitroaniline ($C_6H_6N_2O_2$) + NH_4Cl $\Delta Hrxn$ = -168 MJ/mol

The reaction at the time of the accident was carried out in a 3,000 gallon autoclave under autogenous pressure at about 175° C. Typical pressures during processing are 450 to 550 psig, and are due to the combined vapor pressures of NH_3 and H_2O. The overall reaction is quite exothermic, and normally this heat is removed by water flowing through a jacket placed around the autoclave. For the most part, this reaction has been conducted without incident, with the exception of a reactor explosion that occurred in 1969 in Sauget, IL [2-3]. Although no one was killed, four men were seriously injured. The building containing the reactor was destroyed (see Figure 1). The explosion occurred because of a complication related to a relief system. A rupture disk with a pressure rating of 695 psia leaked into the space before a relief valve placed series with the rupture disk. This compound relief system did not allow the reactor to relieve until pressures exceeded 1,000 psig. Had the relief system functioned at the designed set pressure (~695 psia), the reactor (a 4,000 psig rating) would not have exploded.

During the runaway, the reactor temperature was high enough to initiate a second significant exotherm, the decomposition of nitroaniline. Heating rates in excess of one million BTU/minute occurred at the height of the runaway. The process had operated safely for at least 30 years before this incident. The root cause was traced back to a management decision to override a feed interlock system during a tank repair that eventually led to the mischarging of the reactant o-CNB. More o-CNB than the normal charge was added.

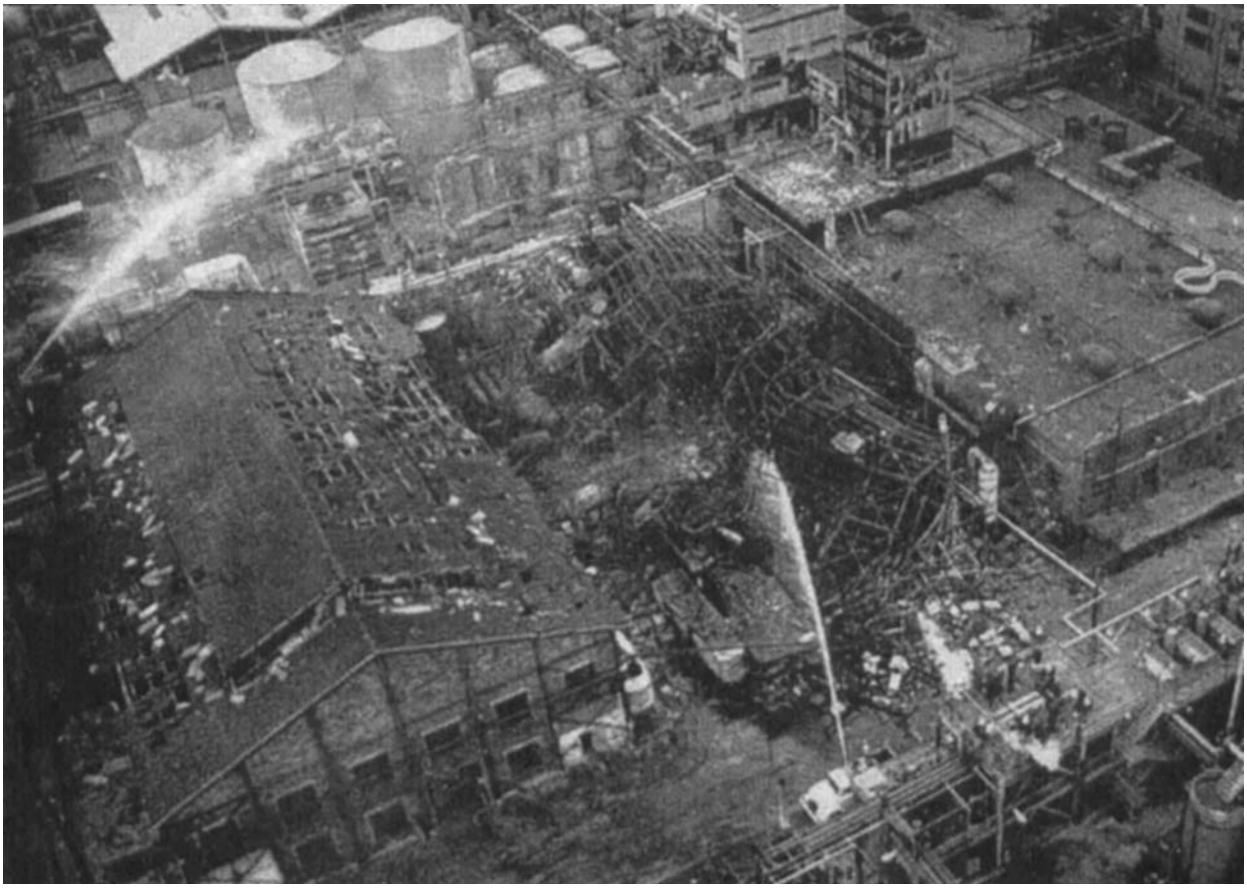


Figure 1. Aerial view of a plant destroyed by a nitroaniline reactor explosion. (from Vincent with permission of AIChE, *Loss Prevention Proceedings, Volume 5*).

It is the purpose of this work to investigate the thermo-kinetics of the reaction using modern adiabatic reaction calorimeters. Our goal is to generate information that can be used by the loss prevention community involved in hazard assessment of complex organic synthesis reactions.

Adiabatic Calorimetry

Over the past 25 years, laboratory equipment specially designed to investigate exothermic reactions has been developed. Two major equipment advancements are the ARC* (accelerating rate calorimeter) and the APTAC™ (automated pressure tracking adiabatic calorimeter). These devices are well known for their ability to track temperature from onset to a runaway, and to measure rates of temperature and pressure rise under adiabatic conditions. Generalized mathematical analysis of experimental data from adiabatic reactors has been presented by Townsend and Tou [4]. Simple first and second order reaction models have been rigorously described. However, most reactions are more complex than simple first or second order, especially if there are more than two reactants involved, or a third body, such as a catalyst, is required. As the work below will demonstrate, simple first order models were inadequate to describe the situation under discussion.

METHODS

Materials

All chemicals were obtained from Aldrich Chemical Company. The following materials were used: ammonium hydroxide Aldrich 22,122-8 (28-30%), 1 chloro-2 nitrobenzene (o-chloronitrobenzene) Aldrich 18,576-0 (99%), ammonium chloride Aldrich 21,333-0 (99.5%), and 2 nitroaniline (o-nitroaniline) Aldrich N978-0 (98%).

Arc Runs

Arc runs were completed on several pure and binary mixtures for the purpose of obtaining vapor-liquid equilibrium data and VLE curves to help estimate binary interaction parameters. Vessel size was 8.6 ml +/- 0.4 ml (standard ARC bombs 1 in i.d.) composed of stainless steel or titanium. The first run shown in Table 1 was with NH_4Cl. Ammonium chloride is a salt that does not liquefy but is readily soluble in water. Standard liquid properties do not exist. Thus, we had to build in properties that treated ammonia chloride as a real liquid. Other runs shown in Table 1 are related to binary interaction parameter estimation for a modified Peng Robinson Equation of State of Mixtures [5].

APTAC Runs

Table 2 contains a summary of important details related to experiments done in the APTAC. In all cases the vessel was composed of titanium and was 130 ml

Table 1. ARC runs completed in this study.

	Run	Quantity, grams	Purpose	Vessel	Comments
1	Pure NH_4Cl	1.5	Vapor-liquid equilibrium check of NH_4Cl against SuperChems databank	Ti	Good Run
2	o-nitroaniline	1.99	VLE	Ti	Bomb ruptured, severe
3	o-nitroaniline	0.5	VLE	SS-316	Good Run
4	NH_4Cl o-nitroaniline	0.387 1	VLE – Binary interaction parameters	Ti	Good Run
5	NH_4Cl H_2O	2 0.68	VLE – Binary interaction parameters	Ti	Good Run
6	o-nitroaniline H_2O	1 0.137	VLE – Binary interaction parameters	Ti	Good Run
7	o-chloronitrobenzene H_2O	1 0.52	VLE – Binary interaction parameters	Ti	Bomb rupture, mild

Vessels Ti – ADL Part #851-3299, 1" i.d., 0.035" wall 1/4" attachment neck, mass 10.4 g.
SS – ADL Part #851-3329, 1" i.d., 0.032" wall 1/4" attachment neck, mass 17 g.

Table 2. APTAC runs completed in this study.

Run	28-30% NH_3 Solution, grams	o-CNB grams	Phi Factor	T onset 1st Exo	Tmax 1st Exo	T end 1st Exo	T onset 2nd Exo
1	40	8	1.19	141.9	161.4	173.3	230.9
2	25	10	1.22	147.2	191.3	203.0	226.4
3	12	20	1.22	147.2	203.4	226.4	243.4
4	14.9	20	1.22	152.2	Ran into 2nd Exotherm		

Table 3. Summary of exotherm information for pure component runs.

Run	Material	T_{MO}	T_{Mmax}	T_{MF}	Phi	Ea/R, K	n (model)	T_{Ao}
1	HCl	350	------	400	2.48	12,800	1	
3	o-NA	260	331	348	8.73	32,700	1.5	241

1. T_{MO} Measured onset temperature measured where self heating rate > 0.02 C/minute.*
2. T_{Mmax} Temperature measured at peak heating rate.
3. T_{MF} Final temperature measured where self heating rate still exceeded 0.02 C/min.
4. T_{AO} Onset temperature for a completely adiabatic system with phi=1.0 (no addition thermal load for the reactor)

* Notation used in this work follows that used in Appendix VI DIERS Bench Scale Apparatus, Fisher, H., et. al., *Emergency Relief Systems Design Using DIERS Technology*, DIERS/AIChE, New York, NY, 1992.

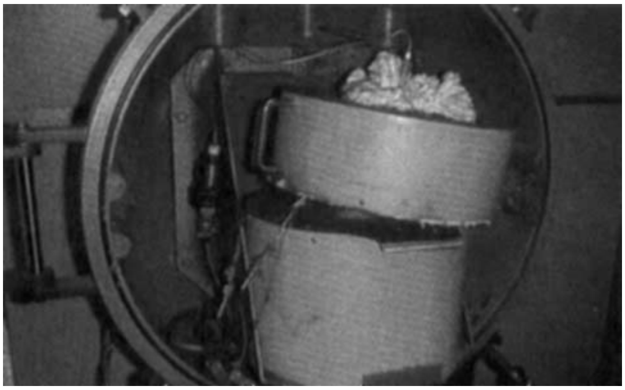


Figure 2. ARC calorimeter after a test of 2 grams of o-nitroaniline in a 8.6 ml Titanium sample bomb.

in size (2.5 inches in diameter). A magnetic Teflon coated stir bar was placed in the bottom of the spherical bomb and stirring was completed by an external magnetic drive rotating at 300 rpm. Heating patterns were set at 2° C/min with 5° C increments followed by a wait and search period of 25 minutes between each increment. When exotherms were detected over 0.05° C/min during the search period, heaters track sample temperature adiabatically. Runs 1 & 2 were with excess NH_3. Run 3 had excess oCNB. Run 1 was very close to ratios used in a process reported by Groggins [1].

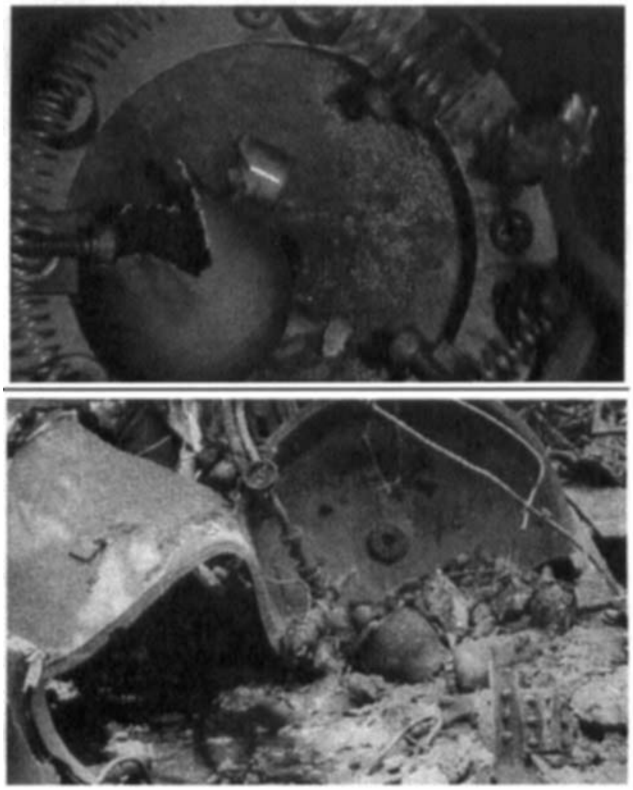
RESULTS

Arc Runs

The violence of a nitroaniline exotherm can be observed in Figure 2. This was the first test where 2 grams of o-NA was added to a 8.6 ml spherical test cell. Figure 3 is a close up of the titanium sample bomb. We see that the destruction is indicative of a deflagration rather than a detonation and note that the real reactor was destroyed in a similar manner, as the adjacent figure shows. Both of these were ductile failures.

Figure 4 shows the temperature and pressure rise that occurs when 1 gram of o-nitroaniline are used in the ARC test cell. This test also contained 0.387 g of NH_4Cl and was specifically done to collect VLE data. However, the figure also demonstrates the extreme self reactivity of o-nitroaniline. The total time window where a significant runaway occurs is less than one minute (between 1,330 and 1,332 minutes). During this period, the maximum pressure rise rate was 3,000 psi/min and the maximum rate of temperature rise was 400° C/min. Analysis of this portion of the data shows an activation energy greater than 50,000 cal/mol with over 300 MJ/kmol of heat released—a very energetic reaction! This activation energy can be compared with di-benzyl toluene which is reported to be 38,500 cal/mol, and with the methanol/acetic anhydride reaction of 11,000 cal/mol.

Figure 5 shows an ARC run for 2 grams of ammonium chloride. Ammonium chloride decomposes to HCl and NH_3 when heated. This process can be seen in the figure up to a temperature of 350° C. The heater is increasing the temperature in five-degree C increments, yet the endothermic reaction causes the temperature to drop during the wait and search mode. At the same time, the pressure of the sample rises due to the endothermic formation of HCl and NH_3. An exothermic reaction was detected at about 350° C. This exotherm lasted for about 100 minutes, increasing the temperature to 400° C (where the ARC was programmed to shut down and cool). The exotherm was probably due to HCl attack on the stainless steel fittings, producing H_2 gas and $FeCl_3$.



Figures 3a and b. Comparison of titanium sample bomb close ups after testing with 2 g o-nitroaniline with the autoclave destroyed in the explosion described above (Photograph from Vincent, with permission from AIChE Loss Prevention Series).

APTAC Runs

Figure 6 shows the heating rates determined with the APTAC runs 1-3. Runs 1 and 2 had excess NH_3 while Run 3 had excess o-CNB. Run 1 represents the normal batch ratios. This data shows a maximum heating rate of 0.1 C/min, well within the heat removal capability of the autoclave cooling system of the full-scale reactor. Runs 2 and 3 show increasing adiabatic temperature rise and maximum heat rate. This is related to the mixture approaching the stoichiometric ratio for complete consumption of both reactants.

The maximum pressures at the final temperatures for the primary reaction exotherm were 436.1, 523.5 and 584 psia for Runs 1 through 3 respectively. The autoclave used to manufacture o-NA had a pressure relief system set for 695 psia. These conditions, based on APTAC data, would not alone create the overpressure needed to trip the pressure relief. The reader is reminded

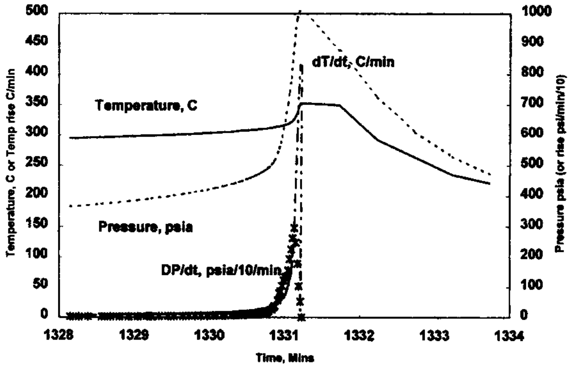


Figure 4. Detailed pressure and temperature curves for an 8.6 ml arc cell containing 1 g of o-nitroaniline and 0.387 grams of NH_4Cl.

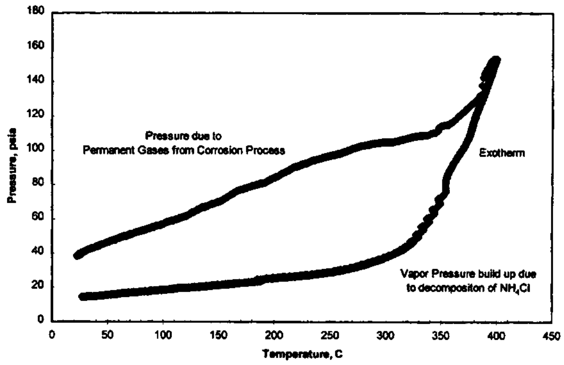


Figure 5. Pressure/temperature results for an ARC run with 2 grams of ammonium chloride.

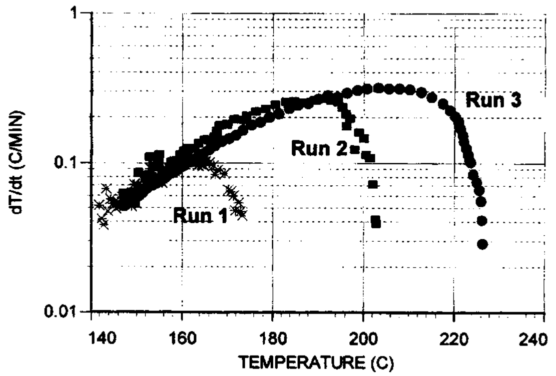


Figure 6. Self heating rates measured for Runs 1-3 using the APTAC (first exotherm).

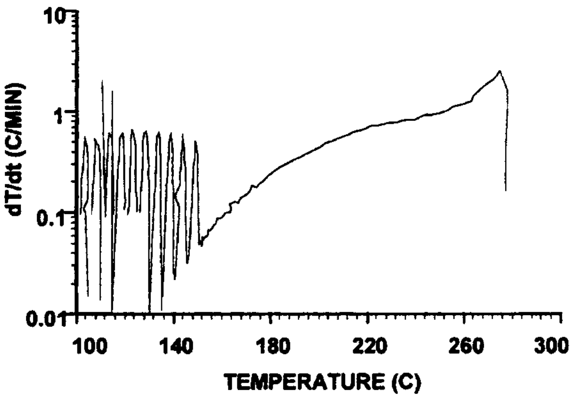


Figure 7. Heating rate information for Run 4.

that the relief system consisted of a rupture disk followed by a spring relief valve. As discussed earlier, the presence of HCl can lead to a corrosive medium and the rupture disk in the real case formed pin holes over time. These pin holes created a compounded pressure blockage that resulted in something much greater than 600 psi (maybe as high as 1,400 psi) before the reliefs opened. The original report claimed that if the relief system had worked as designed, the reactor would have relieved rapidly enough to keep the contents from entering the temperature where o-nitroaniline decomposes.

Figure 7 shows the heating rate for Run 4. The exotherm for the first reaction is great enough to carry over to the decomposition of o-nitroaniline. Because of the violence of this second reaction, it was rapidly quenched at about 260° C in order to prevent rupture of the sample vessel and damage to the calorimeter.

KINETIC MODELS AND USE OF SUPERCHEMS™ TO MODEL RESULTS

The First Exotherm

Significant effort went into the search for kinetic models that would describe all 4 APTAC runs shown above. The goal included matching dT/dt versus 1/T data, as well as pressure versus temperature data. In order to match pressure/temperature data, several binary component runs were done in the ARC to obtain vapor liquid equilibrium data (see Table 1 above). Data from these runs were used for the estimation of binary interaction parameters for most pairs of components used. An example of how well pressure and temperature were matched is shown for Run 2 in Figure 8.

Kinetic Models

Figure 9 shows the results using SuperChems™ to model APTAC experimental result for Runs 1, 2, and 3. The SuperChems simulation used the APTAC mode (heat-wait-search) in its vessel definition. This mode allows for precise heat-wait-search duplication that matches the actual heat-wait-search used experimentally. The kinetic models that were used in this prediction were:

Reaction 1: o-CNB + NH_3 → o-NA HCl
Rate (kmol/m^3 s) = 11,500 exp(-9500/T) $C_{NH_3}^{1.5}\ C_{o\text{-}CNB}^{0.5}$
Reaction 2: HCl + NH_3 → NH_4Cl
Rate (kmol/m^3 s) = 4.8 x 10^7 exp(-12,000/T) $C_{NH_3}^{1}\ C_{HCl}^{1}$
Reaction 3: Decomposition of o-NA → 0.5 N_2 + 1.5 H_2O + $C_6H_3O_{0.5}N$
Rate (kmol/m^3 s) = 8.7 X 10^{14} exp(-25,000/T) $C_{oNA}^{1.5}C_{H_2O}^{1}$

All concentrations are in kmol/m^3. Reaction 3 is discussed in detail below under the second exotherm.

The major difference is that the model for Run 3 predicts a continuous advance into the second exotherm. Examination of the raw data suggests that Run 3 was very close to running into the second

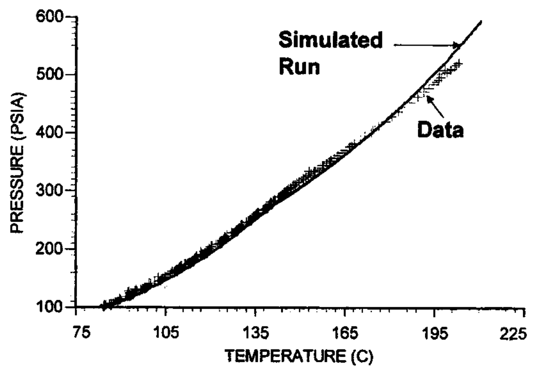


Figure 8. Pressure versus temperature for Run 2 up to end of first exotherm.

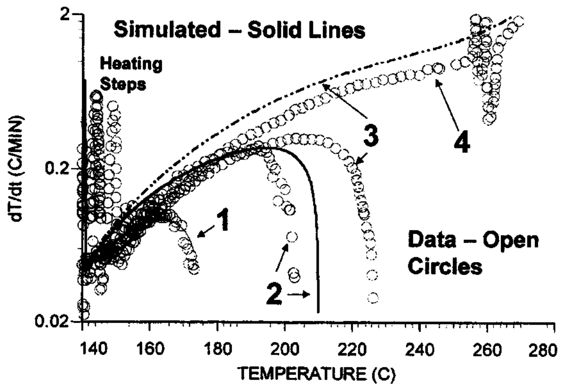


Figure 9. Comparison of dT/dt predicted by kinetic models used in SuperChems simulation of APTAC Runs 1-3.

exotherm. Thus, the thermo-kinetic model predicts the start of the second exotherm at a slightly lower temperature than observed. Reaction 2 is suggested by the corrosion that we observed during Run 3, and the small "offset" observed as Run 3 completes the first exotherm. Although this offset isn't observed in the SuperChems simulations shown in Figure 9, it was quite apparent in our preliminary fits using an Excel Spreadsheet [6] that this offset appears and Reaction 2 is necessary to match experimental data well. Note that towards the end of Run 3, Reaction 3 is beginning to catch on (the inflection in the line). Although this matches Run 4 better than 3, keep in mind that the two runs are different by just 3 grams (+25%) of NH_3 solution (Table 2).

The Second Exotherm

Figure 10 shows an exotherm for pure o-nitroaniline (Run 3 in Table 1). Note that this exotherm was initiated with a rapid change in slope (compared to little change in slope for first order reactions). This observation is often related to autocatalytic reactions where the product accelerates the rate of reaction as the product is produced. In this case, we selected water as the accelerating agent. A related observation was made by Duch, et. al. [7] when they noted that o-nitroaniline onset temperature was almost 40° C degrees lower when an ARC experiment was done in a reaction product mixture rather than with pure Nitroaniline (their product mixture included aqueous ammonia). Our results confirmed these observations. We see in Table 2 that the onset temperature for the second exotherm can be as low as 226.4° C (Duch et al report 229.5° C for their mixture), when the reaction mixture was present. The matching of the pressure temperature curves for these runs required additional experiments, including GC-MS analysis. The production of N_2 was verified by running o-NA in argon and sampling the gas space after reaction. The GC-MS analysis did not reveal what was the dominant organic product, as there were over 20 trace species (parts per thousand and parts per million detected), including isomers of nitroaniline, chloronitrobenzene and nitrobenzene. We elected to create a partial oxidation product (see Reaction 3 above) such that the pressure/temperature cooling curves matched reasonably well after the full simulation.

Figure 11 summarizes the conditions leading to reactor runaway and a o-NA decomposition. These estimates were made using SuperChems and the kinetic models reported above. The simulated reactor was an iron vessel with 3,000 gallon capacity and mass of about 12.5 tons (11,500 kg). The initial charge was constant at 6,800 kg. We see in this figure that when the mass ratio was 5 to 1 aqueous ammonia solution to o-chloronitrobenzene, the plant would always be in a safe region. This helps explains why the plant had made nitroaniline for 40 years without incident. We also see that the change in initial reactant charge ratios initiated the second runaway. The minimum ratio where this can occur is about 3 to 1 ammonia solution to o-CNB. Another demonstration on this figure is that maximum T_{END} for the first exotherm occurs right at the stoichiometric ratio of the two primary reactants. The message here is straight forward. Evaluation of multiple reactant exothermic system must include thermo-kinetic runs at stoichiometric ratios in order to establish that secondary exothermic decomposition reactions cannot occur.

CONCLUSIONS

1. Hazard Analysis based on thermo-kinetic analysis of organic based reactions should include evaluations on all products.
2. Hazard Analysis based on thermo-kinetic analysis of organic based reactions should include evaluations at the stoichiometric amounts of the reactants.
3. A nitro-aniline reactor explosion was successfully modeled and experimentally confirmed using adiabatic calorimetry and SuperChems.
4. It was found that three successive reactions were required, one of which was autocatalytic, in order to predict the behavior.
5. This work demonstrates the importance of studying reactivity under upset conditions, such as loss of temperature control, wrong additions etc. Adiabatic calorimetry and kinetic modeling are a powerful combination in predicting the likely outcome of such upset conditions.

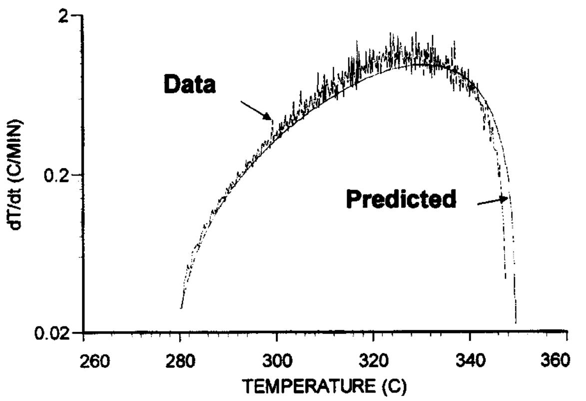


Figure 10. o-NA decomposition done in ARC (Run 3) Phi=9.3.

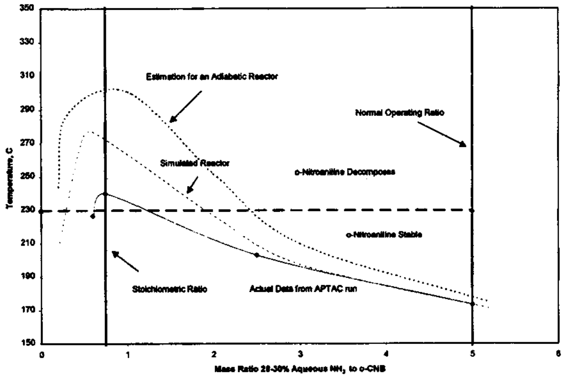


Figure 11. Temperature of no return (defined here as the T_{END} of the first exotherm) as a function of mass ratio of initial reactants.

ACKNOWLEDGMENTS

The authors acknowledge the work of Dan Onea, in conducting the physical test program involved. Daniel Nguyen, ADL, is acknowledged for his assistance on the SuperChems instruction and analysis. Willey and Rodriques are also grateful to ADL for donating equipment time and expertise in this analysis.

LITERATURE CITED

1. **Groggins, P.H.,** *Unit Processes in Organic Synthesis, 5th Edition*, pp 465-468, McGraw-Hill, New York, NY, 1958.
2. **Vincent, G.C.**, "Rupture of a Nitroaniline Reactor," *Loss Prevention, Vol. 5*, AIChE, New York, NY, pp 46-52, 1971.
3. **Willey, R.J.**, "Seminar on a Nitroaniline Reactor Rupture," SACHE teaching case study, AIChE, New York, NY, 1994.
4. **Townsend, D.I. and J.C. Tou**, "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter," *Thermochimica Acta,* 37, pp 1-30, 1980.
5. **Saini, R.**, "A Modified Peng-Robinson Equation of State with Binary Parameters Predicted from a Group Contribution Method," Ph.D. Thesis, Northeastern University, Boston, MA, 1999.
6. **Rodriques, F.M.**, MS Thesis, Northeastern University, Boston, MA, 2000.
7. **Duch, M.W., K. Marcali, M.D. Gordon, C.J. Hensler, and G.J. O'Brien**, *Plant/Operations Progress*, 1, 1, pp 19, 1982.