

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

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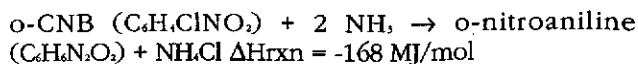
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*Exothermic reaction processing must be concerned with potential consequences when heat released by the reaction exceeds that removed by the reactor coolant system, a situation known commonly as a runaway reaction. We have investigated a complicated 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<sub>3</sub> solution 26° Be (28 to 30% NH<sub>3</sub> by wt %) and o-chloronitrobenzene.



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<sub>3</sub> and H<sub>2</sub>O. 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<sup>®</sup> (accelerating rate calorimeter) and the APTAC<sup>™</sup> (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<sub>4</sub>Cl. 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 <sub>4</sub> Cl	1.5	Ti	Vapor-liquid equilibrium check of NH <sub>4</sub> Cl against SuperChems databank
2	o-nitroaniline	1.99	Ti	Bomb ruptured, severe
3	o-nitroaniline	0.5	SS-316	Good Run
4	NH <sub>4</sub> Cl o-nitroaniline	0.387 1	Ti	VLE – Binary interaction parameters
5	NH <sub>4</sub> Cl H <sub>2</sub> O	2 0.68	Ti	VLE – Binary interaction parameters
6	o-nitroaniline H <sub>2</sub> O	1 0.137	Ti	VLE – Binary interaction parameters
7	o-chloronitrobenzene H <sub>2</sub> O	1 0.52	Ti	VLE – Binary interaction parameters

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 <sub>4</sub> 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 <sub>MO</sub>	T <sub>Mmax</sub>	T <sub>MF</sub>	Phi	Ea/R, K	n (model)	T <sub>Ao</sub>
1	HCl	350	-----	400	2.48	12,800	1	
3	o-NA	260	331	348	8.73	32,700	1.5	241

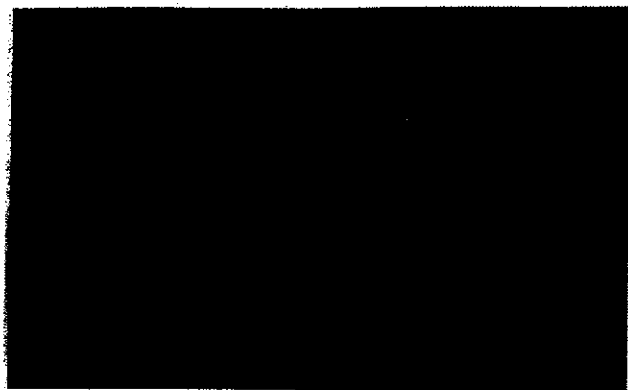
1. T<sub>MO</sub> Measured onset temperature measured where self heating rate > 0.02 C/minute.\*

2. T<sub>Mmax</sub> Temperature measured at peak heating rate.

3. T<sub>MF</sub> Final temperature measured where self heating rate still exceeded 0.02 C/min.

4. T<sub>Ao</sub> 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<sub>3</sub>. Run 3 had excess oCNB. Run 1 was very close to ratios used in a process reported by Groggins [1].

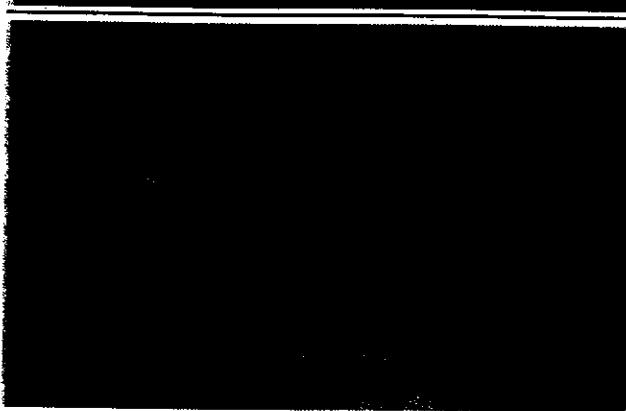
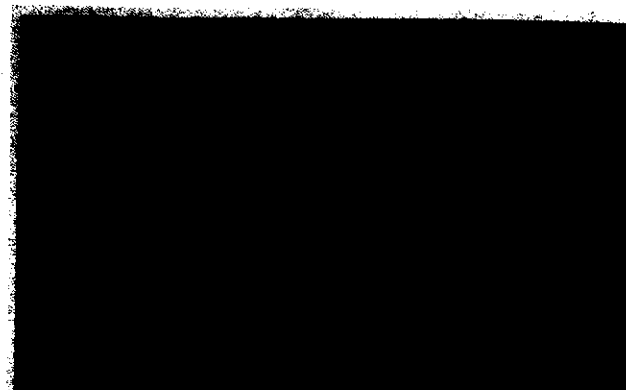
## RESULTS

### 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<sub>4</sub>Cl 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<sub>3</sub> when heated. This process can be seen in the figure up to a temperature of 350° C. The heater is



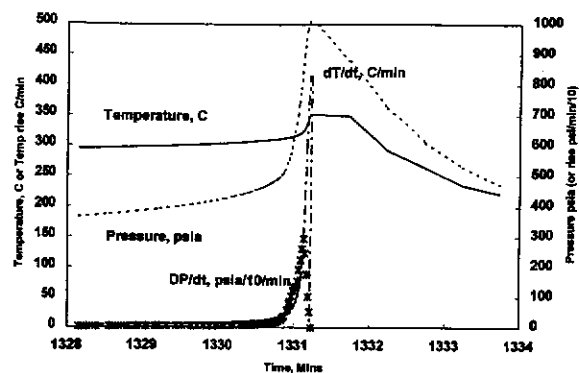
**Figures 3a and b.** Comparison of titanium sample bomb close ups after testing with 2 g o-nitroaniline with the autoclave destroyed in the explosion described above (Photograph from Vincent, with permission from AIChE Loss Prevention Series).

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<sub>3</sub>. 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<sub>2</sub> gas and FeCl<sub>2</sub>.

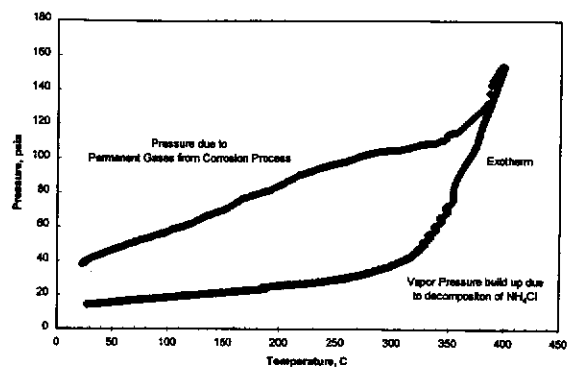
### APTAC Runs

Figure 6 shows the heating rates determined with the APTAC runs 1-3. Runs 1 and 2 had excess NH<sub>3</sub>, 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.

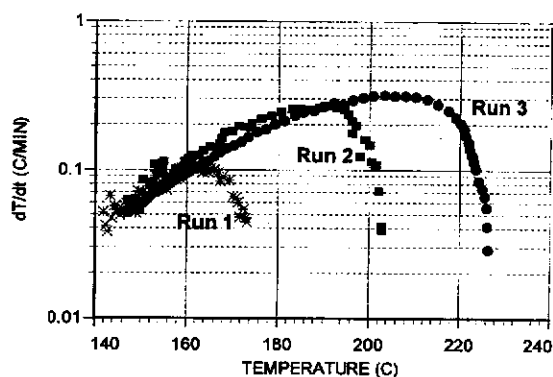
The maximum pressures at the final temperatures for the primary reaction exotherm were 436.1, 523.5 and 584 psia for Runs 1 through 3 respectively. The autoclave used to manufacture o-NA had a pressure relief system set for 695 psia. These conditions, based on APTAC data, would not alone create the overpressure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



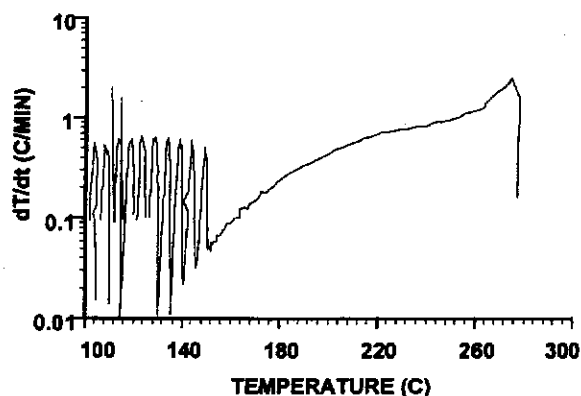
**Figure 4.** Detailed pressure and temperature curves for an 8.6 ml arc cell containing 1 g of o-nitroaniline and 0.387 grams of NH<sub>4</sub>Cl.



**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 SUPERCHEMSTM 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 SuperChemsm™ to model APTAC experimental result for Runs 1, 2, and 3. The SuperChemsm 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:  $\text{o-CNB} + \text{NH}_3 \rightarrow \text{o-NA HCl}$

Rate ( $\text{kmol/m}^3 \text{ s}$ ) =  $11,500 \exp(-9500/T) C_{\text{NH}_3}^{1.5} C_{\text{o-CNB}}^{0.5}$

Reaction 2:  $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$

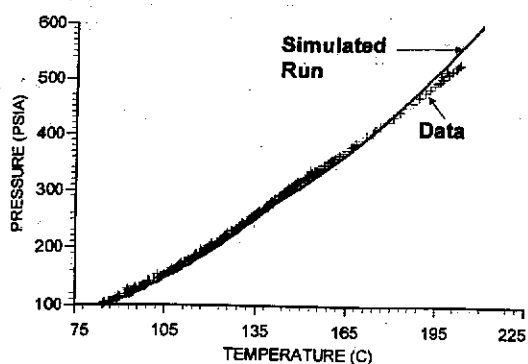
Rate ( $\text{kmol/m}^3 \text{ s}$ ) =  $4.8 \times 10^7 \exp(-12,000/T) C_{\text{NH}_3}^1 C_{\text{HCl}}^1$

Reaction 3: Decomposition of o-NA  $\rightarrow 0.5 \text{ N}_2 + 1.5 \text{ H}_2\text{O} + \text{C}_6\text{H}_5\text{O}_3\text{N}$

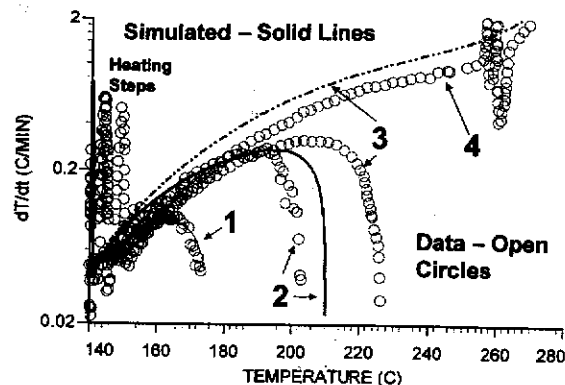
Rate ( $\text{kmol/m}^3 \text{ s}$ ) =  $8.7 \times 10^{14} \exp(-25,000/T) C_{\text{o-NA}}^{1.5} C_{\text{H}_2\text{O}}^1$

All concentrations are in  $\text{kmol/m}^3$ . 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  $\text{NH}_3$  solution (Table 2).

### The Second Exotherm

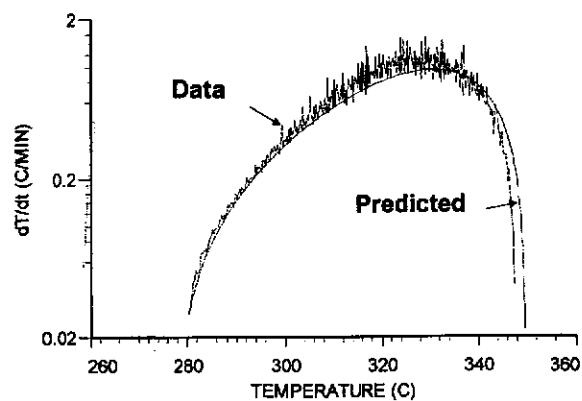
Figure 10 shows an exotherm for pure *o*-nitroaniline (Run 3 in Table 1). Note that this exotherm was initiated with a rapid change in slope (compared to little change in slope for first order reactions). This observation is often related to autocatalytic reactions where the product accelerates the rate 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  $\text{N}_2$  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.

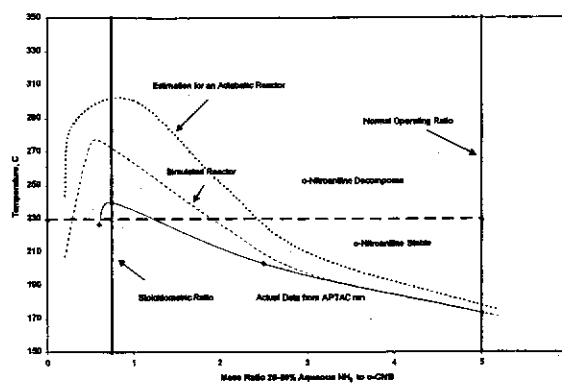
Figure 11 summarizes the conditions leading to reactor runaway and a *o*-NA decomposition. These estimates were made using SuperChems and the kinetic models reported above. The simulated reactor was an iron vessel with 3,000 gallon capacity and mass of about 12.5 tons (11,500 kg). The initial charge 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 explain 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  $T_{\text{END}}$  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  $T_{no}$  of the first exotherm) as a function of mass ratio of initial reactants.

#### ACKNOWLEDGMENTS

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