



## Thermal hazard assessment of nitrobenzene/dinitrobenzene mixtures

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### ABSTRACT

During the production of nitrobenzene by an adiabatic nitration process, the main byproducts are mono and dinitrophenols as well as 2,4,6-trinitrophenol (picric acid) and 1,3-dinitrobenzene. The byproducts can become concentrated if a distillation step to remove high boiling point impurities is used. In the present work, representative samples of nitrobenzene containing 20–30% dinitrobenzene and less than 1% dinitrophenol, 1% picric acid, and 1% sodium hydroxide were tested by Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) to investigate their thermal stability relative to the pure substances. The DSC thermal curves for pure nitrobenzene and the various nitrobenzene–dinitrobenzene mixtures exhibited exothermic activity from about 300 °C to 500 °C and enthalpy changes of about  $-2.5 \times 10^3 \text{ J g}^{-1}$ , which is very energetic. The impurities (dinitrophenol, picric acid, and sodium hydroxide) had no significant effect on the DSC results. During the ARC experiments, the various nitrobenzene–dinitrobenzene mixtures were found to be less thermally stable than pure nitrobenzene and pure dinitrobenzene, with exotherms beginning in the 263–280 °C temperature range. Analysis of ARC data indicates that short-term exposure of nitrobenzene mixtures containing up to 20 mass% dinitrobenzene to temperatures up to 208 °C should not pose a serious runaway reaction hazard.

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### 1. Introduction

During the industrial production of nitrobenzene, the main reactant, benzene, is nitrated using an acid solution composed of sulfuric acid, nitric acid, and water. The reactant mixture consists of two phases (organic and aqueous) that must be stirred together to promote the desired nitration reaction. In a typical adiabatic nitration process, the reaction mixture is heated to temperatures of less than 150 °C. The main byproducts of the reaction are mono and dinitrophenols as well as 2,4,6-trinitrophenol (picric acid) and 1,3-dinitrobenzene [1–3].

The product mixture is fed to a separator, which separates the aqueous acid phase from the crude nitrobenzene. The crude nitrobenzene is washed in a number of stages, including with a dilute base (e.g., sodium hydroxide) [4], and introduced into a distillation column to remove ‘light’ (i.e., low boiling point) impurities. Depending on the desired purity, the product may be distilled once more in a second column, under vacuum, to remove ‘heavy’ (i.e., high boiling point) impurities.

The byproducts formed during nitrobenzene production can become more concentrated, especially during the removal of ‘heavy’ impurities through a distillation step. Through the latter

step, it is not unusual to concentrate dinitrobenzene up to 20 mass% in the ‘bottoms’ (i.e., the liquid which is found in the column’s sump, located at the bottom of the distillation column, below the bottom tray).

Although pure nitrobenzene is stable at temperatures well above those of normal process conditions, it is known that the presence of impurities or contaminants can significantly lower the decomposition temperature of nitro-organic compounds [5–7]. In particular, there has been a reported case of an industrial explosion at a nitrobenzene production facility when the ‘bottoms’ of a ‘heavies’ batch column became over-heated [8].

In a proactive effort to ensure the safe design of their processes, Noram Engineering and Constructors Ltd., a Vancouver, BC-based company which designs chemical plants for the production of nitrobenzene, embarked on a joint project with the Canadian Explosives Research Laboratory (CERL) to investigate the thermal stability of mixtures of nitrobenzene containing high concentrations of reaction byproducts. The results of the investigation are reported here.

### 2. Experimental

#### 2.1. Materials

Noram Engineering provided four samples, and their compositions are shown in Table 1. The samples were prepared by vacuum

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**Table 1**

Composition of samples submitted by Noram Engineering.

Sample #	Nitrobenzene (%)	Dinitrobenzene (%)	2,4-Dinitrophenol (%)	Picric acid (%)	Sodium hydroxide (%)
1	80.00	20.00	0	0	0
2	78.77	19.69	0.76	0.77	0
3	78.36	19.59	0.80	0.77	0.48 <sup>a</sup>
4	70.00	30.00	0	0	0

<sup>a</sup> The sodium hydroxide did not completely dissolve in the sample.

evaporating nitrobenzene containing 200 ppm dinitrobenzene initially. Additional components were added to Samples #2 and #3 after the distillation. The compositions of Samples #2 and #3 were selected to represent worst-case scenario byproduct and sodium hydroxide contamination levels in process, while the compositions Samples #1 and #4 were selected to evaluate the effect of dinitrobenzene on the thermal stability of nitrobenzene in the absence of other process byproducts.

It should be noted that, at the time of testing, the sodium hydroxide in Sample #3 had formed a sludge in the bottom of the sample vial, and the sludge disappeared into a short-lived suspension when the vial was shaken. The suspension was tested in the DSC. For the ARC experiment on Sample #3, 0.01 g of solid sodium hydroxide was placed in the ARC vessel before loading the sample.

A fifth sample, dubbed Sample #5 hereafter, was generated at CERL by mixing 1.4310 g of Sample #1 and 1.5385 g of Sample #4.

Nitrobenzene, ACS reagent grade ( $\geq 99.0\%$  purity), was obtained from Sigma–Aldrich. 1,3-dinitrobenzene,  $\geq 97.0\%$  purity, was also obtained from Sigma–Aldrich.

## 2.2. Differential scanning calorimetry (DSC)

DSC (differential scanning calorimetry) is one of the most widely used calorimetric techniques for evaluating the thermal hazards of reactive chemicals [9]. DSC experiments were performed on a TA Instruments Q2000 DSC equipped with a standard cell. The DSC instrument was calibrated for temperature and heat flow using standard methods [10,11]. All DSC experiments were performed with the sample placed in a glass ampoule. Each ampoule was made from a Kimax<sup>®</sup> capillary tube, 1.6–1.8 mm O.D., 0.2 mm wall thickness, and was approximately 8 mm in length when sealed. Each ampoule was loaded with 0.2–0.4 mg of sample. Sealed ampoules were wrapped in silver foil to improve thermal contact with the DSC sensors. The DSC cell was ramped at  $5\text{ }^{\circ}\text{C min}^{-1}$  from  $40\text{ }^{\circ}\text{C}$  to either  $525\text{ }^{\circ}\text{C}$  or  $550\text{ }^{\circ}\text{C}$ , and the DSC cell was purged at  $50\text{ mL min}^{-1}$  with dry nitrogen.

## 2.3. Accelerating rate calorimetry (ARC)

The ARC apparatus is a commercial adiabatic calorimeter that is used to assess the thermal hazard potential of energetic chemicals or materials [12,13]. For each ARC experiment, 1–3 g of sample material was placed in a spherical, carbon steel vessel (0.1% carbon), and the vessel was subsequently attached to the apparatus to form part of a closed, leak-tight system. The system was verified to be leak-tight before each experiment by monitoring the pressure while the system was pressurized to 2 MPa with dry air. Carbon steel vessels were chosen because it is the material of construction for process equipment in Noram Engineering's nitrobenzene manufacturing processes.

The experiments were performed in an atmosphere of dry air initially at ambient pressure. For the initial experiments, the ARC procedure of heat-wait-search was used. During this procedure, the temperature of the vessel was raised from an initial temperature of  $100\text{ }^{\circ}\text{C}$  to a maximum temperature of  $350\text{ }^{\circ}\text{C}$  in  $5\text{ }^{\circ}\text{C}$  increments (the

heat period). For each temperature increment, the vessel was maintained adiabatic during both a wait period of 15 min (which allows the dissipation of thermal transients) and a search period of 10 min. During the search period, the ARC system searches for exothermic behaviour in the vessel. The system recorded an exotherm whenever the sample's self-heating rate exceeded a chosen threshold value of  $0.02\text{ }^{\circ}\text{C min}^{-1}$ . The temperature at which the self-heating rate first exceeded  $0.02\text{ }^{\circ}\text{C min}^{-1}$  was recorded as the detected onset temperature.

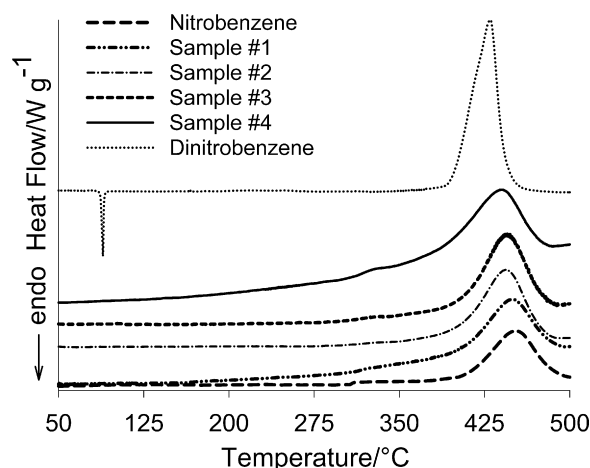
Isothermal ARC experiments were performed at  $163\text{ }^{\circ}\text{C}$  and  $208\text{ }^{\circ}\text{C}$ , the maximum normal operating temperature of a nitrobenzene vacuum distillation column and the temperature of process steam, respectively. The isothermal ARC experiments were performed with the same instrument settings as the heat-wait-search experiments, except that the initial temperature was set to either  $163\text{ }^{\circ}\text{C}$  or  $208\text{ }^{\circ}\text{C}$ . For all isothermal experiments, the initial search period was 6000 min. The instrument terminated each experiment when the vessel temperature exceeded  $350\text{ }^{\circ}\text{C}$  or the self-heating rate exceeded  $1\text{ }^{\circ}\text{C min}^{-1}$ .

In order to help interpret the ARC pressure data, it should be noted that a sample vessel, the tubing, and the fittings have a total volume of approximately 10 mL when empty.

## 3. Results and discussion

### 3.1. DSC

The DSC thermal curves are summarized in Fig. 1. For pure nitrobenzene and Samples #1–#4, the DSC traces are all very similar to one another. Each of the samples exhibited mild exothermic activity between  $300\text{ }^{\circ}\text{C}$  and  $350\text{ }^{\circ}\text{C}$ , after which there is a relatively large exotherm. The peak of the larger exotherm occurs at approximately  $450\text{ }^{\circ}\text{C}$ . The initially mild exothermic activity between  $300\text{ }^{\circ}\text{C}$  and  $350\text{ }^{\circ}\text{C}$  is slightly enhanced in Sample #4, which may be caused by its elevated level of dinitrobenzene. The exotherms produce enthalpy changes of about  $-2.5 \times 10^3\text{ J g}^{-1}$ , which is very



**Fig. 1.** DSC traces for samples heated at  $5\text{ }^{\circ}\text{C min}^{-1}$  in glass micro-ampoules.

**Table 2**  
Summary of heat-wait-search accelerating rate calorimeter (ARC) results.

Sample	Mass tested (g)	Mass loss (%)	ARC onset (°C)	$P_{\max}$ (MPa)	$P_{\text{res}}^a$ (MPa)	Maximum rate (°C min <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	ln(Z/min <sup>-1</sup> )	$r^2$
Nitrobenzene	1.0117	21.8	316	2.2	1.9	0.34	N/A	N/A	–
Nitrobenzene	1.0098	6.0	325	2.2	0.40	0.78	234 ± 42	40.5 ± 8.2	0.93
Dinitrobenzene	1.0110	11.0	310	0.4	0.67	1.0	303 ± 13	59.2 ± 2.6	0.99
Sample #1	1.0415	17.8	274, 280, 288	2.9	0.70	0.62	147.5 ± 0.5	28.0 ± 0.1	0.99
Sample #2	1.0122	22.7	270, 276, 282, 288, 295	3.1	0.76	0.53	164.6 ± 0.7	31.4 ± 0.2	0.98
Sample #3	1.0108 <sup>b</sup>	21.9	280, 287, 294	3.0	0.82	0.93	244 ± 33	48.3 ± 6.8	0.99
Sample #4	0.9988	21.6	268, 285, 296, 303	2.9	0.80	0.56	165 ± 14	31.3 ± 2.8	0.98
Sample #5:	2.9695	6.9	263, 272, 282	4.2	1.1	1.0	194 ± 1.5	38.3 ± 0.3	0.96

<sup>a</sup> The residual pressure,  $P_{\text{res}}$ , is the observed pressure at the end of the run, after the ARC cooled to room temperature.

<sup>b</sup> Includes 0.0103 g of sodium hydroxide, which was added to the ARC vessel prior to loading the sample.

energetic. The impurities in Samples #2 and #3 did not appear to have much effect on the onset, shape, and magnitude of the exotherms. In ref. [7] an enthalpy change of  $-2.8 \times 10^3 \text{ J g}^{-1}$  was observed for pure nitrobenzene, which is very similar to this work, but a higher onset temperature of 380 °C was observed. The higher observed onset temperature is likely due to the much heavier high-pressure crucibles used as sample holders in [7], which may have reduced sensitivity to the weak initial exothermic activity observed in this work.

Dinitrobenzene exhibited two peaks: an endothermic melting peak with an extrapolated onset temperature of 88 °C and an enthalpy change of  $102 \text{ J g}^{-1}$ , and an exothermic decomposition peak with an onset temperature of 373 °C and an enthalpy change of  $-3.7 \times 10^3 \text{ J g}^{-1}$ . It is thus more energetic than nitrobenzene but also appears to be more thermally stable in the DSC, as indicated by its higher onset temperature. In reference [7], the observed DSC onset temperature for pure 1,3-dinitrobenzene was 270 °C, which is over 100 °C lower than the onset observed in this work, while an enthalpy change of  $-3.5 \times 10^3 \text{ J g}^{-1}$  was observed, which was similar to the enthalpy change observed.

The reason for the discrepancy in onset temperatures is not known. The DSC experiment on dinitrobenzene was performed in duplicate in this work, and the results of the duplicate experiments were nearly identical to one another. The DSC onset temperature of 270 °C observed in [7] is inconsistent with the onset temperature of 310 °C observed in the ARC in this work (Table 2), since ARC onset temperatures are typically significantly lower than those observed in the DSC. The results in this work are more consistent with the results reported in [7] for 1,4 dinitrobenzene, which had an onset of 350 °C and an enthalpy change of  $-3.7 \times 10^3 \text{ J g}^{-1}$ .

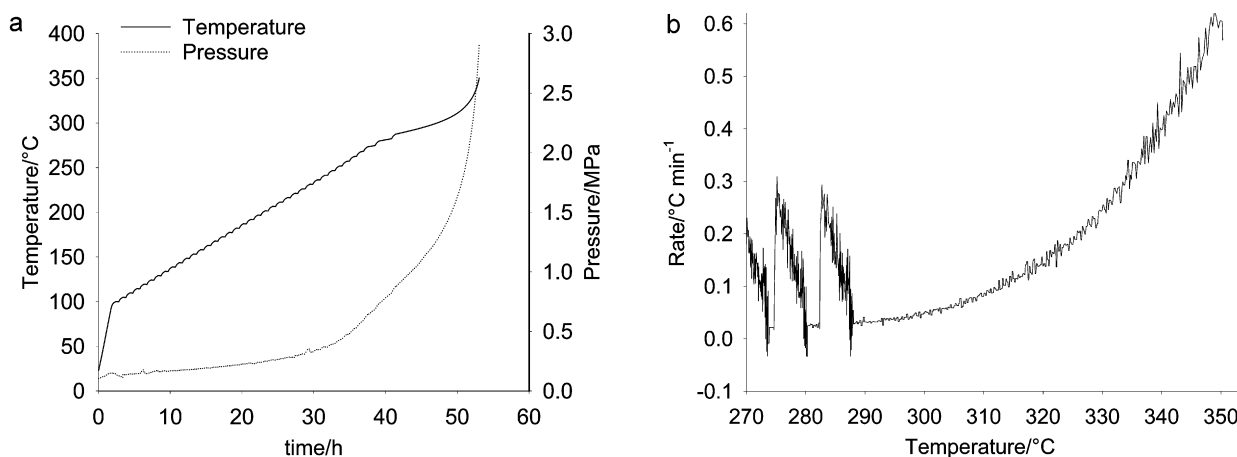
It should be noted that for the curves in Fig. 1, the DSC baseline was not flat throughout the experiments. Linear regression was

performed on the data from 100 °C to 300 °C to calculate the slope of the baseline, and this result was used to correct the DSC data throughout each experiment.

### 3.2. ARC

The heat-wait-search ARC results are summarized in Table 2, and a typical result is illustrated in Fig. 2a and b. Samples #1–4 exhibited similar trends to one another in the ARC calorimeter. Minor exotherms are exhibited beginning at 263–280 °C, but the self-heating rate during these initial exotherms does not consistently remain above the selected threshold for an exotherm ( $0.02 \text{ °C min}^{-1}$ ). As a result, the ARC returns to heat-wait-search mode several times until the final exotherm is observed (i.e., until it reaches a temperature above which the self-heating rate always exceeds  $0.02 \text{ °C min}^{-1}$ ). The final exotherm occurs somewhere between 287 °C and 303 °C. The self-heating rate gradually accelerates until the ARC reaches 350 °C.

The experiment on Sample #5 (which used a larger 3 g sample mass) and the experiment on pure dinitrobenzene were terminated when the self-heating rate exceeded  $1 \text{ °C min}^{-1}$ , which occurred before the instrument reached 350 °C. All of the other ARC experiments terminated at 350 °C because the ARC was programmed to automatically terminate experiments at this temperature. Samples #1–#4 exhibited lower onset temperatures than both pure nitrobenzene and pure dinitrobenzene, indicating that either the impurities or the combination of the two nitrobenzenes reduces nitrobenzene's thermal stability. It is somewhat unusual that pure dinitrobenzene exhibited a significantly higher (by about 50–75 °C) onset temperature than pure nitrobenzene in the DSC, whereas it exhibited a slightly lower (5–11 °C) onset temperature in the ARC. The relative positions of the onset temperatures observed



**Fig. 2.** (a) Temperature and pressure history for a heat-wait-search ARC experiment on Sample #1. (b) Self-heating rate vs temperature for a heat-wait-search ARC experiment on Sample #1.

**Table 3**  
Summary of isothermal accelerating rate calorimetry (ARC) results.

Sample	Mass tested (g)	T (°C)	Mass loss (%)	ARC onset (°C)	$P_{\max}$ (MPa)	$P_{\text{res}}^a$ (MPa)	Maximum rate (°C min <sup>-1</sup> )
Sample #2	1.8826	163	0.69	N/A	0.20	0.10	0
Sample #3	1.7495 <sup>b</sup>	208	0.71	N/A	0.53	0.18	0

<sup>a</sup> The residual pressure,  $P_{\text{res}}$ , is the observed pressure at the end of the run, after the ARC apparatus had cooled to room temperature.

<sup>b</sup> Includes 0.0198 g of sodium hydroxide, which were added to the ARC vessel prior to loading the sample.

in the ARC results appear to be more consistent with the relative peak temperatures observed in the DSC. It is likely that there is weak exothermic activity occurring in nitrobenzene below its ARC-detected onset temperature, but that the activity is below the detectable threshold of the ARC. Since this weak exothermic activity is enhanced when dinitrobenzene is added, as indicated by the DSC results, it becomes just barely detectable in the 263–300 °C range when the nitrobenzene/dinitrobenzene mixtures are tested in the ARC.

As described in ref. [12], approximate kinetics can be derived from the self-heating rate data by assuming a zero-order reaction (i.e., that the reaction rate is independent of concentration). If this assumption holds true, a plot of the natural logarithm of the self-heating rate as a function of inverse temperature will yield a straight line. The parameters  $Z$  and  $E_a$  for the well-known Arrhenius equation, shown below, can be derived from the intercept and the slope of the line.

$$\text{Reaction Rate} = Z \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where  $Z$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is the temperature in Kelvin.

Plots of self-heating rate versus inverse temperature were constructed for all of the heat-wait-search ARC experiments (for an example, see Figure 2b). From Table 2, it can be seen that the kinetics of the decomposition of Sample #2 and #4 are identical within the error estimates. The decomposition kinetics of Sample #1 are slightly different than that of Samples #2 and #4, but its predicted reaction rates are within  $\pm 20\%$  of Sample #2 and #4 in the 300–350 °C range. This is reflected in the fact that the maximum self-heating rates achieved for Samples #1, 2, and 4 were similar, namely 0.5–0.6 °C min<sup>-1</sup>.

Sample #3 achieved a higher self-heating rate of 0.9 °C min<sup>-1</sup>, which suggests that the kinetics of the reaction may be different from that of the others despite having a similar onset temperature. This is reflected in the Arrhenius parameters,  $E_a$  and  $\ln(Z)$ , which are very different from of Samples #1, #2, and #4. It should also be noted that the Arrhenius parameters were calculated using data between 294 °C and 321 °C because the data above 321 °C did not appear to be linear on the natural logarithm of the self-heating vs. inverse temperature plot, further suggesting that the decomposition kinetics of this sample are different from the others.

The isothermal ARC results are summarized in Table 3. A steady pressure was observed during the isothermal experiment at 163 °C, which indicates that the sample did not decompose into gaseous products. Based on the ideal gas law, one would expect a 0.05 MPa increase in pressure when heating the air trapped in the system from a 25 °C to 163 °C, yielding a total system pressure of 0.15 MPa. Some additional increase in pressure due to the vapor pressure of nitrobenzene would also be expected. The observed system pressure was 0.18 MPa (average) at 163 °C, suggesting that the sample was essentially inert over the two-day-long experiment (although conversion of nitrobenzene to its nitrobenzene isomer, could be occurring [14]). In general, the amount of mass lost during an ARC experiment indicates the mass of sample that has decomposed into gaseous products. Based on the observed mass loss of 0.69%, very lit-

tle decomposition appears to have occurred after two days at 163 °C.

A slight, gradual pressure increase was observed during the isothermal experiment at 208 °C. Based on the ideal gas equation, one would expect a 0.06 MPa increase in pressure when heating the air trapped in the system from 21 °C to 208 °C, and a pressure increase of 0.1 MPa due to the vapor pressure of nitrobenzene (boiling point approximately 212 °C). If the sample were completely inert, the total pressure in the system would have been 0.26 MPa. The maximum observed pressure was 0.53 MPa, which is a 0.27 MPa higher than expected for the inert system, which suggests that a small amount of decomposition products were created during the five-day long experiment.

Some isomerization and combination reactions may occur during nitrobenzene decomposition, producing non-volatile products, but the main products of nitrobenzene decomposition are expected to include N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, and NO, N<sub>2</sub>O, NO<sub>2</sub>, and H<sub>2</sub>O. Most of these products are volatile at room temperature (21 °C in the lab), except for H<sub>2</sub>O (water). NO and NO<sub>2</sub>, which are soluble in water, may therefore also be present in a condensed phase. Since the tubing which connects the ARC vessel to the pressure transducer is not heated, the few milligrams of water that may have formed would likely have condensed outside of the ARC vessel. Based on the observed mass loss of 0.71%, very little decomposition appears to have occurred after five days at 208 °C.

It is a peculiar result that the same mass loss was observed for both Sample #2, which was inert, and Sample #3, which decomposed to a small extent (as evidenced by the residual pressures). The mass loss observed for Sample #2 is especially peculiar since the residual pressure was equal to the initial pressure, which suggests that no volatile product formation occurred. However, it should be noted that the mass lost was very small (13 mg), and may be attributed a small droplet of nitrobenzene having condensed in the fittings or the tubing connecting the ARC vessel to the pressure transducer. This explanation is consistent with previous ARC experiments performed in-house on water in a titanium vessel, when greater mass losses were observed even though the water was inert.

The maximum pressure observed for Sample #3 is several times atmospheric pressure. Thus, although the sample did not go to thermal runaway, the results show that any process where this mixture would occur at 208 °C would either have to resist such elevated pressures or provide a means of safely venting the overpressure. Emergency shutdown of the heat source upon the loss of vacuum to a nitrobenzene vacuum-distillation column is also advisable as a precautionary measure to avoid generating elevated pressures.

### 3.3. Extrapolation of ARC results to lower temperatures and larger quantities

The mass of nitrobenzene handled in a manufacturing plant is many orders of magnitude larger than the 3 g or less used in the ARC apparatus. In addition, process temperatures are well below the lowest onset temperatures observed. As a result, extrapolation

**Table 4**  
Parameters used in the calculation of the  $\phi$  factor.

Substance	Source	Heat capacity ( $\text{J g}^{-1} \text{ } ^\circ\text{C}^{-1}$ )	Mass (g)
Steel	Fittings and strap	0.50 [16]	14.5
Carbon steel	ARC vessel	0.465 [16]	14.6
Nitrobenzene	Sample	1.4 [15]	3.0

of the ARC data to larger quantities and lower temperatures is necessary for the results to be applicable to manufacturing processes.

The isothermal ARC data indicate that the Sample #3 should be stable for at least a five-day storage period at 208 °C if the temperature does not rise. It should be noted that the isothermal ARC results do not necessarily imply that the system would actually stay at the isothermal temperature if the mixture were held in a bulk storage container. The temperature of a system rises whenever the rate of heat input and heat generation exceeds the rate of heat loss. In the case of the nitrobenzene/dinitrobenzene mixtures, heat is generated by chemical reaction. The amount of heat generated as a function of temperature can be estimated from the self-heating rate data obtained in the heat-wait-search ARC experiments. To extrapolate ARC self-heating rate data to large systems, the observed adiabatic self-heating rate data must be corrected for (i.e., multiplied by) the  $\phi$  factor, which can be estimated by Eq. (2) below:

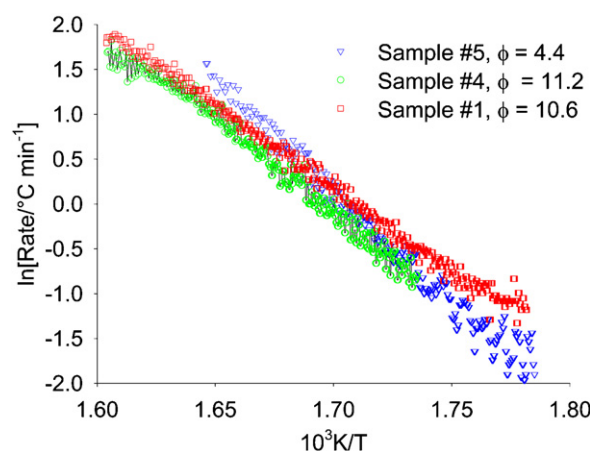
$$\phi = \frac{m_s c_s + m_c c_c}{m_s c_s} \quad (2)$$

where  $m_s$  and  $m_c$  are the mass of the sample and the container, respectively, and  $c_s$  and the  $c_c$  are the specific heat capacities of the sample the container, respectively. The significance of the  $\phi$  factor is discussed in detail in Reference [12]. In a large container, the  $\phi$  factor approaches a value of 1.0, which means that most of the energy released during a chemical reaction heats the sample material and only a small proportion of the energy heats the container. In the ARC instrument, the  $\phi$  factor is typically much greater than 1.0, which means that a significant proportion of the energy released during chemical reaction heats the container.

The  $\phi$  factor was estimated using the parameters shown in Table 4. Note that in the ARC instrument, the mass of the container includes the mass of the carbon steel vessel, the Swagelok® fittings used to secure the vessel to the ARC manifold, and the strap used to secure the sample thermocouple to the vessel. In a previous study, it has been shown that the mass of the fittings and strap do not contribute their full mass to the effective  $\phi$  factor, and the proportion of their effective contribution scales as a complicated function of the sample's and vessel's mass [17]. The calculations presented in this paper are based on the assumption that the full mass of strap and fittings contribute to the  $\phi$  factor, so the calculated  $\phi$  factor is expected to be higher than in the actual ARC experiments. As a result, the corrected self-heating rates should provide rates that are slightly higher than in an actual large-scale adiabatic system.

The heat capacity of the mixture was approximated to be that of pure nitrobenzene at 20 °C (see Table 4). When this heat capacity is used, the  $\phi$  factor for the ARC vessel is 10.6 for the heat-wait-search experiment on Sample #1, 11.0 for the heat-wait-search experiment on Sample #4, and 4.4 for the heat-wait-search experiment on Sample #5.

A plot of the  $\phi$  corrected natural logarithm of the initial self-heating rate versus inverse temperature obtained from the adiabatic portion of the heat-wait-search ARC experiments performed on Sample #1, Sample #4 and Sample #5 is shown in Fig. 3. As shown in the Figure, the plots are reasonably linear ( $r^2 > 0.96$ ). The self-heating rate data were multiplied by the  $\phi$  factors discussed above, and the natural logarithm of the initial self-heating rate versus inverse temperature was computed for each data set. Lin-



**Fig. 3.** Measured self-heating rates corrected for (i.e., multiplied by)  $\phi$  as a function of inverse temperature.

ear regression was performed on the resultant data sets, and the best-fit line parameters are shown below.

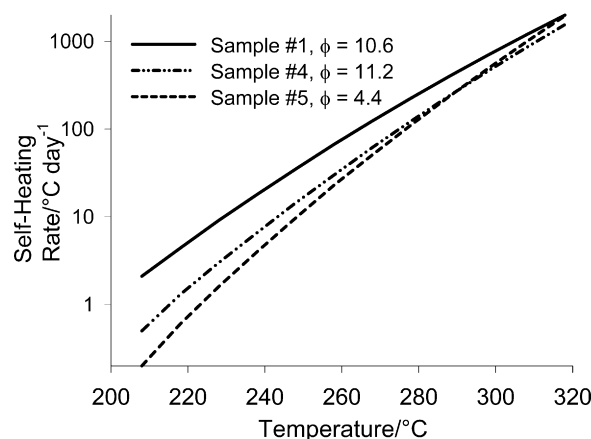
$$\ln(\text{Rate}/^\circ\text{C min}^{-1}) = 34.91 - \frac{20593}{T}, \quad \phi = 11 \text{ (Sample\#4)} \quad (3)$$

$$\ln(\text{Rate}/^\circ\text{C min}^{-1}) = 30.32 - \frac{17737}{T}, \quad \phi = 10.6 \text{ (Sample\#1)} \quad (4)$$

$$\ln(\text{Rate}/^\circ\text{C min}^{-1}) = 39.78 - \frac{23340}{T}, \quad \phi = 4.4 \text{ (Sample\#5)} \quad (5)$$

where Rate is the adiabatic self-heating rate ( $^\circ\text{C min}^{-1}$ ) and  $T$  is the temperature (Kelvin).

Eqs. (3), (4) and (5) can be used to predict the self-heating rate of a sample at any temperature, in the absence of heat losses, assuming that no change in mechanism (i.e., constant kinetics) occurs over the temperature range of the predictions. Predictions from Eqs. (3), (4) and (5) are summarized in Fig. 4. If heat losses are neglected, the regression results suggest that a large, perfectly insulated container initially at 208 °C would self-heat by 2.1 °C or less after one day. For a 20 m<sup>3</sup> vessel, which would correspond to a large storage tank, the natural cooling capacity of the tank corresponds to a limiting safe self-heating rate of 2.6 °C day<sup>-1</sup>. This safe self-heating rate should be representative and conservative, based on a review of several hazard assessment techniques [18]. Thus, temporary loss of vacuum control during nitrobenzene distillation, which could result in short-term exposure of nitrobenzene mixtures containing up to 20 mass% of dinitrobenzene to temperatures up to 208 °C,



**Fig. 4.** Predicted adiabatic self-heating rate versus temperature of nitrobenzene/dinitrobenzene mixtures at plant-scale.

would not pose a runaway reaction hazard. It should be noted that, if the mixtures were initially at 238 °C, the results indicate that they might self-heat to thermal runaway in less than two days. Thus, the results suggest that the initial temperature of the nitrobenzene mixtures and the rate of heat loss are critical parameters affecting the stability of the system in the temperature range above 208 °C.

#### 4. Conclusions

It was found that the presence of dinitrobenzene in Samples #1–#4 and the additional impurities (dinitrophenol, picric acid, and sodium hydroxide) in Sample #2 and #3 had no significant effect on the onset temperature, shape, and magnitude of the exothermic peaks observed in the DSC, as compared to pure nitrobenzene. Pure dinitrobenzene, on the other hand, exhibited a higher onset temperature for decomposition and a greater enthalpy change than pure nitrobenzene.

In contrast to the DSC results, the heat-wait-search ARC experiments on the nitrobenzene–dinitrobenzene mixtures (Samples #1–#4 and #5) indicated that these mixtures were less thermally stable than either of the pure substances. The mixtures exhibited minor exotherms beginning in the 263–280 °C temperature range, with the final exotherm occurring at an onset temperature somewhere between 288 °C and 303 °C. Pure nitrobenzene exhibited an onset temperature between 316 °C and 325 °C, and pure dinitrobenzene an onset temperature of 310 °C. Either the impurities or the combination of the two nitrobenzenes in the mixtures reduced nitrobenzene's thermal stability.

Based on analysis of the isothermal ARC experiment at 208 °C on Sample #3 and extrapolated self-heating rate data from heat-wait-search experiments, it is expected that nitrobenzene–dinitrobenzene mixtures would not rapidly self-heat at 208 °C for several days or longer under process conditions. Thus, temporary loss of vacuum control during nitrobenzene distillation, which could result in short-term exposure of nitrobenzene mixtures containing up to 20 mass% dinitrobenzene to temperatures up to 208 °C, should not pose a serious runaway reaction hazard. For industrial nitrobenzene vacuum-distillation columns, providing a means of safely venting overpressure and emergency shutdown of the heat source upon the loss of vacuum are advisable precautionary measures.

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#### References

- [1] A.A. Guenkel, Nitrobenzene and Nitrotoluene, in: J.J. McKetta, W.A. Cunningham (Eds.), *Encyclopedia of Chemical Processing and Design*, Marcel Dekker, 1990.
- [2] M. Dugal, Nitrobenzene and Nitrotoluenes, *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th ed. October, John Wiley & Sons, Inc., 2005.
- [3] P.A. Quadros, N.M.C. Oliveira, C.M.S.G. Baptista, Continuous adiabatic industrial benzene nitration with mixed acid at a pilot plant scale, *Chem. Eng. J.* 108 (2005) 1–11.
- [4] J.-L. Gustin, Runaway reaction hazards in processing organic nitro compounds, *Org. Proc. Res. Dev.* 2 (1998) 27–33.
- [5] J.L. Gustin, Influence of trace impurities on chemical reaction hazard, *J. Loss Prev. Process Ind.* 15 (2002) 37–48.
- [6] S. Chervin, G.T. Bodman, R.W. Barnhart, Decomposition of energetic chemicals contaminated with iron or stainless steel, *J. Hazard. Mater.* 130 (2006) 48–52.
- [7] Y.S. Duh, C. Lee, C.C. Hsu, D.R. Hwang, C.S. Kao, Chemical incompatibility of nitrocompounds, *J. Hazard. Mater.* 53 (1997) 183–194.
- [8] Japan Science and Technology Agency, Failure Knowledge Database, <http://shipipai.jst.go.jp/en/Detail?fn=0&id=CC1000093&>, last accessed on Jan. 12, 2010.
- [9] D.J. Frurip, T. Elwell, Effective use of differential scanning calorimetry in reactive chemicals hazard evaluation, *Process Saf. Prog.* 26 (2007) 51–58.
- [10] ASTM E967-03 Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers, ASTM International, West Conshohocken, PA, USA.
- [11] ASTM E968-02 Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters, ASTM International, West Conshohocken, PA, USA.
- [12] D.I. Townsend, J.C. Tou, Thermal hazard evaluation using an accelerating rate calorimeter, *Thermochim. Acta* 37 (1980) 1–30.
- [13] Arijit Bhattacharya, A general kinetic model framework for the interpretation of adiabatic calorimeter rate data, *Chem. Eng. J.* 110 (2005) 67–78.
- [14] T.B. Brill, K.J. James, Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives, *Chem. Rev.* 93 (1993) 2667–2692.
- [15] P. Pacor, Applicability of the DuPont 900 DTA apparatus in quantitative differential thermal analysis', *Anal. Chim. Acta* 37 (1967) 200–208.
- [16] R.H. Perry, D. Green (Eds.), *Perry's Chemical Engineers Handbook*, sixth ed., McGraw-Hill, 1984.
- [17] M. Braithwaite, N. Davies, W.C. Evans, P.D. Lightfoot, Simple finite element modelling applied to the problems in energetic materials characterisation: design of pyrotechnic devices and explosives calorimetric studies, in: *Proceedings of the 29th International Pyrotechnics Seminar*, Westminster, CO, USA, 2002.
- [18] S. Tharmalingam, Assessing runaway reactions and sizing vents, *Chem. Eng. (August)* (1983) 33–41.