

## DIFFERENTIAL SCANNING CALORIMETRY OF HAZARDOUS MATERIALS: 4-NITRO-*m*-CRESOL AND *p*-NITROPHENOL\*

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### ABSTRACT

In order to help determine the cause of an explosion of 4-nitro-*m*-cresol (PNMC) held at 155°C, we have used differential scanning calorimetry (DSC) to study the thermal properties of this compound and of *p*-nitrophenol (PNP) which had been manufactured in the same plant as PNMC.

Pure PNMC begins an exothermic decomposition at 230°C, but upon extended aging in microbombs at 155°C for periods of up to one week, the PNMC progressively disappears while the exothermic decomposition temperature is reduced to 160°C. If the gases produced during the aging process are allowed limited venting, formation of the reactive intermediate does not occur and the decomposition temperature does not drop.

Although our results indicated that sealing the containers caused a more rapid deterioration of the PNMC, it is important to note that the explosion took place in a vented vessel and that the circumstances of the actual plant experience were not duplicated by our experiments.

Pure PNP exothermically decomposes at 260°C. Aging studies in microbombs at 155°C show no decomposition to occur, while aging at 175°C causes decomposition, but the resulting drop in the exothermic decomposition temperature is not below 200°C.

Electron spin resonance studies show that the radicals produced during the aging of PNMC are graphitic, whereas those produced by PNP are nitrogenous.

### INTRODUCTION

In October 1969 an explosion, followed by a flash fire, occurred in a 3000 gallon vented tank containing 1500 gallons of 4-nitro-*m*-cresol (PNMC) at an indicated temperature of 154°C. A summary of the work done to investigate the cause of the accident has been reported elsewhere<sup>1</sup>.

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We have used the Perkin-Elmer DSC 1B to study the thermal properties of PNMC and *p*-nitrophenol (PNP). The latter compound was necessary for comparison with PNMC since the plant had successfully produced PNP for nine months before the conversion to PNMC manufacture. The explosion occurred during the startup of manufacture after the PNMC had been accumulating in the tank for three days. The operating temperature in this part of the plant was nominally 135°C but, because of difficulties in the lines leading to the tank, had been heated up to 154°C.

We therefore decided to study the effect of aging on both compounds, and, because of a comment in a paper by Cecil and Koerner<sup>2</sup> that the production of reactive gases in nitroaromatic decompositions could enhance the decomposition rate in confined systems, to make the comparison between sealed and vented conditions.

## EXPERIMENTAL

### Materials

*p*-Nitrophenol. — PNP ("pure"), 99.7% by cryoscopic analysis; PNP ("sample A"), 72.1% by gas chromatography; PNP ("sample B"), 72.8% by gas chromatography.

4-Nitro-*m*-cresol. — PNMC ("pure"), 99.7% by cryoscopic analysis; PNMC ("sample C"), 79.0% by gas chromatography; PNMC ("sample D"), 30.1% by gas chromatography.

Samples A, B, C, and D were plant samples.

### Procedure

Samples were encapsulated in either microbombs or hermetically-sealed aluminum or gold pans. The monel microbombs were based on the design of Freeburg and Alleman<sup>3</sup>.

Once encapsulated and weighed, the samples were placed in ovens for aging. Upon being removed and cooled to ambient temperature, they were reweighed to

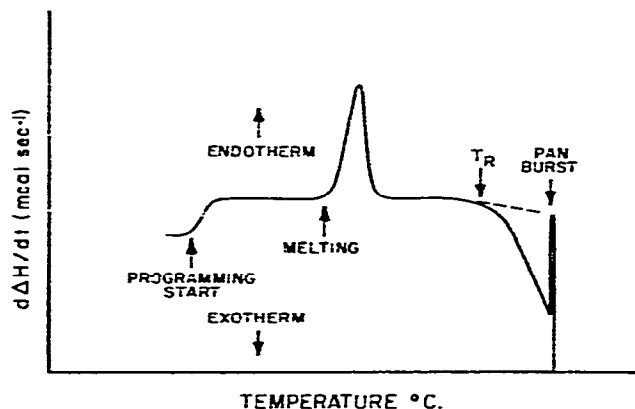


Fig. 1. Sketch of a typical DSC curve.

determine if leakage had occurred. When an aging study was completed, all aged samples and an unaged control were run on the DSC through the decomposition range. It was found convenient to reencapsulate the contents of the microbomb samples in aluminum or gold pans for best results, since baseline reproducibility is poor with the microbombs. In general a given thermal curve was marked by a melting endotherm, an exotherm, and in some cases, a sharp deflection due to sample pan rupture (see Fig. 1).

The temperature of the onset of the exotherm,  $T_R$ , was taken as the first deviation from the baseline. Increasing baseline curvature with increasing temperature led to some difficulty in assigning this value with precision.

The use of the heat of fusion as a method for determining the amount of parent compound remaining was convenient, but certainly increasingly less accurate as the concentration of parent compound decreased. However, the absence of any fusion peak, which we took to be evidence of complete disappearance of the parent, was found by gas chromatography to correspond, at most, to 10% of the original compound remaining. This is probably because the rise of the concentration of impurities soluble in the melt becomes limited by the formation of polymeric reaction products which are insoluble, thereby not affecting the melting behavior. Thus, the lowering of the melting point is not progressive, although the area under the melting curve may ultimately fall to zero.

For studying the effects of partial venting, it was necessary to use tightly capped stainless steel vials which allowed light gases to vent while preventing excessive volatilization of the parent compound. DSC runs were made on samples subsequently encapsulated in aluminum.

For purposes of obtaining the heats of decomposition, we tried the method suggested by Duswalt<sup>4</sup>, wherein the sample is encapsulated in aluminum after dispersion on an inert support such as Cab-O-Sil. We were not successful in preventing pan rupture during the exotherm. Two runs were successfully made using monel microbombs which did survive without leakage. The data from these runs were analyzed by a computer program which give the heat of reaction, rate constants and the Arrhenius equation for first-order kinetics.

Electron spin resonance studies were performed on a Varian 4500 Series ESR Spectrometer with a 9-in. magnet. Studies were made both in a heated cavity, starting with unaged sample, and at room temperature with aged samples, both sealed and vented.

## RESULTS AND DISCUSSION

Our plan was to carry out aging studies at 133°C and 155°C, the design and the feed tank temperatures prior to the explosion, respectively. In Fig. 2, the DSC results for a PNMC set aged at 155°C are shown. The samples are approximately the same size. The decrease of the area under the fusion peaks as the samples are progressively aged is due to decomposition reaction and not to weight loss. The  $T_R$  values

DSC RUNS

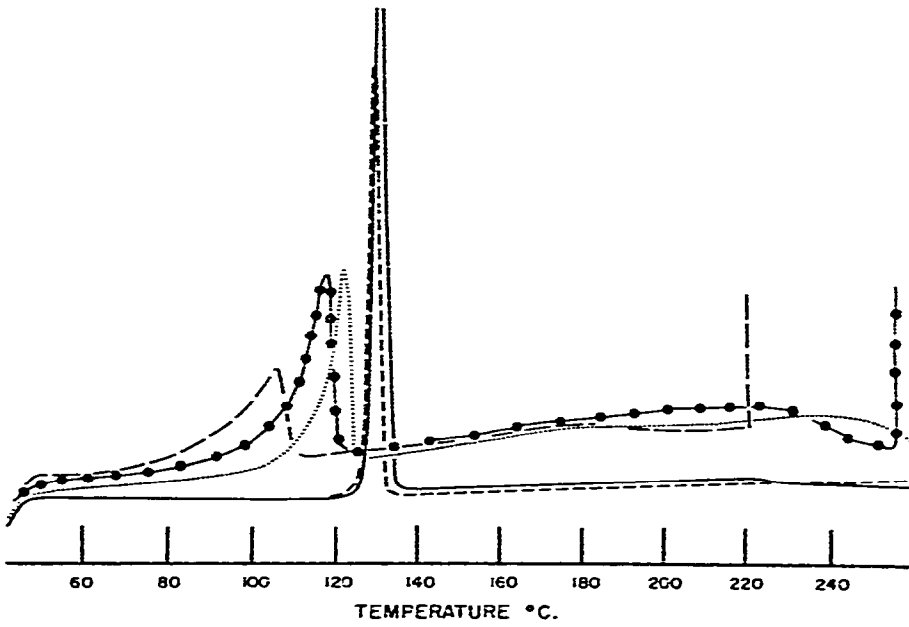


Fig. 2. Typical DSC curves for pure PNMC aged at 155°C. Heating rate 10°/min in sealed Al. Unaged control——; aged 0.2 days ----; aged 2.9 days ······; aged 4.0 days—●—●—; aged 5.1 days——.

also drop with continued aging as will be shown later. By contrast, Fig. 3 shows that aging sealed samples of PNP at 155°C is essentially without effect although most of

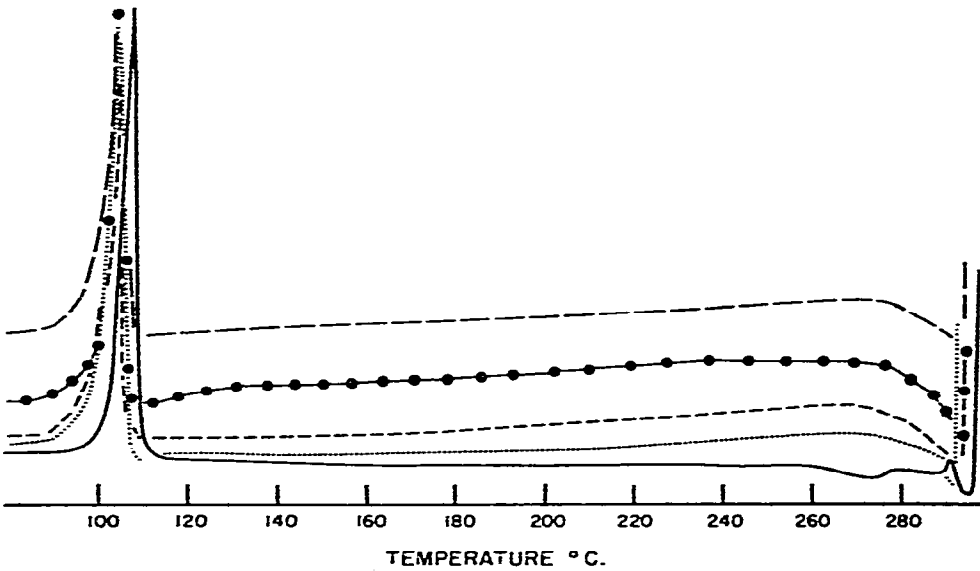


Fig. 3. Typical DSC curves for pure PNP aged at 155°C. Heating rate 10°/min in sealed Al. Unaged control ——; aged 2 days ······; aged 3 days ----; aged 7 days—●—●—; aged 9 days——.

the samples melt slightly lower than the unaged control. Figs. 4 and 5 summarize the effect of aging at 155 and 133 °C on the disappearance of PNMC, and the lowering of  $T_R$ , respectively. It is clear that no decomposition occurs at 133 °C. On the other hand, the reaction which occurs at 155 °C leads to a loss of PNMC with the probable formation of an intermediate which appears to lower the activation energy of the exothermic decomposition.

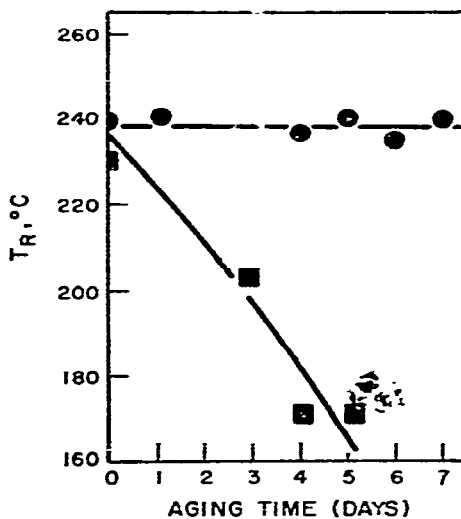
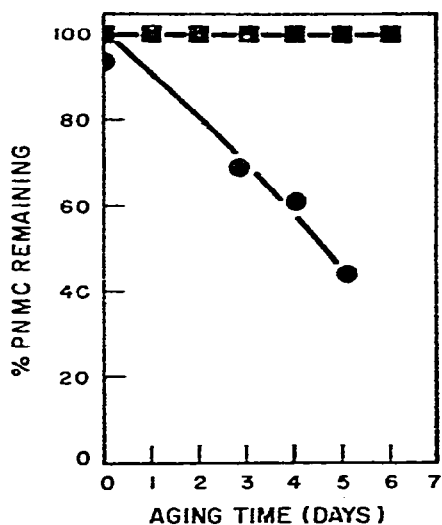


Fig. 4. Effect of aging in sealed containers on amount of PNMC remaining. ■, at 133 °C; ●, at 155 °C. Fig. 5. Effect of aging in sealed containers on  $T_R$  of PNMC. ●, at 133 °C; ■, at 155 °C.

In Fig. 6, results obtained in gold pans are included with those obtained in aluminum in a first order plot. For the straight line portion, the rate constant  $k = 5.3 \times 10^{-2} \text{ day}^{-1}$ , which gives a  $t_{50\%}$  of 13 days. The results with gold discount the possibility that the aluminum containers catalyze the decomposition. In other

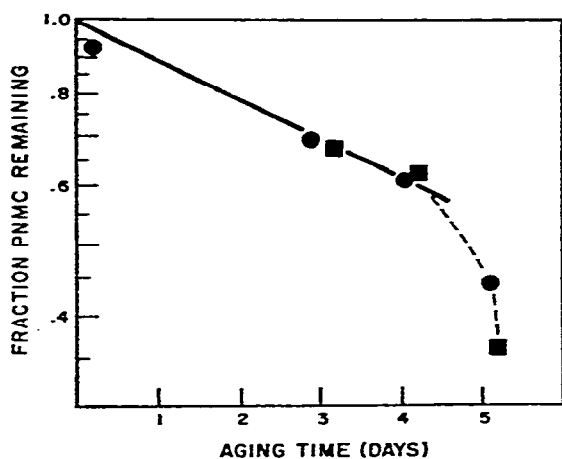


Fig. 6. First order kinetics plot. Pure PNMC aged at 155 °C. ●, sealed Al; ■, sealed Au.

series, we have confirmed that the downturn is real and that no PNMC survives after the sixth day. The lowest  $T_R$  which we have observed is 160°C.

Table I gives the results of the elemental analysis of a series of PNMC samples aged in stainless steel microclaves at 155°C. No evidence of PNMC was found after 48 h of aging. No gross change is seen to occur in the overall composition, although the analyses suggest a condensation polymerization involving the loss of water and occasional loss of nitrogen. The ultimate product is a hard, black, intractable solid.

TABLE I  
ELEMENTARY ANALYSIS OF PNMC RESIDUES FROM THE MICROCLAVE STUDY

Aging time (h)	C (%)	H (%)	N (%)
48	61.6	4.00	8.27
120	57.13	3.75	7.34
144	62.13	4.07	8.83
168	58.79	3.83	8.55
Theoretical values	54.9	4.6	9.15
Theory - H <sub>2</sub> O	62.2	3.7	10.4

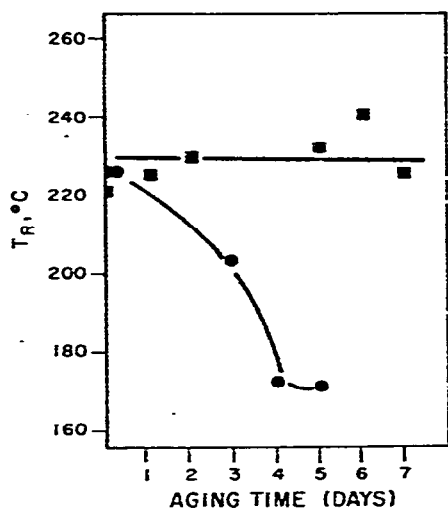


Fig. 7. Effect of aging pure PNMC at 155°C in sealed vs. partially restricted containers on the  $T_R$ . ●, sealed; ■, partially restricted.

The result of PNMC aging at 155°C in partially vented stainless steel containers is contrasted with the result in sealed containers in Fig. 7. Apparently, gases which are produced in the early stages of the decomposition are needed to sustain the continuous conversion to the intermediate species required for the "autocatalysis" of the subsequent exothermic decomposition.

Aging studies on PNP at 155°C produced no significant effect on the  $T_R$  as shown in Fig. 3. When PNP was aged in sealed containers at 175°C, a reduction of

the  $T_R$  value was obtained, generally leveling in a few days at 220°C. In one case, a  $T_R$  of approximately 200°C was observed after extensive aging.

Selected samples from various parts of the process were examined to establish the effect of process impurities on the stability of both PNP and PNMC. Some typical results are given in Table II. It is well known that the stability of nitroaromatics can be adversely affected by impurities. The Table shows that such is the

TABLE II  
EFFECT OF PROCESS IMPURITIES ON  $T_R$

PNP			PNMC		
Sample	Purity (%)	$T_R$ (°C)	Sample	Purity (%)	$T_R$ (°C)
Pure	99.7	260	Pure	99.7	240
A	72.1	230	C	79.0	193
B	72.8	220	D	30.1	168

case for both PNMC and PNP. The significance of the difference between the two is that the  $T_R$  of PNMC can be dropped into the range of operation of the process by either aging or impurities, which does not happen with PNP. Deason, Koerner and Munch<sup>5</sup> have noted that the addition of carbon impurity to PNP does not decrease the stability since the carbon is less readily oxidized than the PNP itself. If we can equate carbon with tarry process materials, then we would expect that the less stable PNMC would be affected less by impurities than the PNP, which is not the case. In fact the reactions are probably different as will be shown in our description of the ESR results.

For the analysis of the heat and kinetics of the exothermic PNMC decomposition, we did manage to obtain two completed DSC curves in monel microbombs. Since the baselines did not close the curves, we had to arbitrarily close them, so that both the accuracy and precision are open to question. One of the samples was a plant sample of 98.1% purity which had behaved similarly to pure PNMC in aging studies. It was aged in the DSC for 16 h at 180°C prior to the run. For each analysis, about twenty equally spaced points were taken for the program previously mentioned. The results are given in Table III. At 155°C, the extrapolated rate constant for the

TABLE III  
HEAT OF DECOMPOSITION AND ARRHENIUS CONSTANTS FOR PNMC

	$\Delta H$ (kcal.mole <sup>-1</sup> )	$A$ (sec <sup>-1</sup> )	$\Delta E$ (kcal.mole <sup>-1</sup> )
Pure	68	$5 \times 10^{17}$	53.5
Plant (98.1%)	88	$4 \times 10^{12}$	39.5

aged plant sample is  $2.4 \times 10^{-3}$  day<sup>-1</sup>, and for the pure sample  $2.0 \times 10^{-5}$  day<sup>-1</sup>, which shows that the aging has indeed accelerated the reaction rate some hundred

fold. More important, perhaps, is that the rate constant for the disappearance of PNMC in the 155°C aging experiments is  $5.3 \times 10^{-2} \text{ day}^{-1}$ , considerably faster than either of these. This result is consistent with the hypothesis that the low-temperature reaction (or reactions) is qualitatively different to the high-temperature exothermic reaction.

The electron spin resonance results give some insight into the differences between PNP and PNMC, as well as between sealed and vented aged samples. When pure PNP was heated above its melting point in the ESR cavity, a spectrum of three lines of nearly equal intensity was observed with a hyperfine coupling of  $\sim 8.4$  gauss. This spectrum is typical of a nitrogen radical. Further heating to and at 180°C did not cause any intensification of the radical concentration. Pure PNMC showed a weak signal at room temperature. Heating to 150°C did not appreciably increase the signal, but above 150°C the radical concentration increased. At 180°C, a continuous increase in radical concentration began to occur and the experiment was stopped for fear of explosion. A single line spectrum with  $g = 2.0035$  and a peak-to-peak width of  $\sim 4$  gauss was observed. Such a spectrum corresponds more to a char or graphitic radical, and is certainly not a nitrogen radical.

A series of samples of pure PNMC, aged from one to six days at 155°C in stainless steel microbombs, was examined at room temperature. The same radical was observed as in the heating experiment, with the concentration increasing with aging to the fifth day and no change between the fifth and sixth days. The radical concentration increased by a factor of a hundred between the first and fifth days. A sample of PNMC char, obtained by heating PNMC through its exotherm, showed the same signal. Another series of PNMC samples aged at 155°C in vented stainless steel vials showed the same signal, but decreased in intensity from the second to the fifth day, with the strongest signal being approximately one-fiftieth the intensity of the char.

The ESR results are in agreement with the DSC results on the differences in the effects of aging PNP and PNMC, and on the drastic effect that sealing the system has on the autocatalysis.

## CONCLUSIONS

From the DSC results, and a knowledge of the events leading up to the explosion, one can construct a logical hypothesis about the reasons for the PNMC explosion. One can speculate that, even though the vessel was vented, the initial charge, upon striking hot surfaces, began relatively rapid deterioration; that the polymers which then formed separated from the melt, sticking to the walls or floating in the melt as separate phases; that, once formed, these masses, retaining decomposition gases long enough for them to react with the substrate, behaved as though they were effectively sealed off from the vent, allowing the acceleration of the decomposition. The temperature may then have risen considerably above the indicated temperature in these isolated phases. Finally, as the  $T_R$  was reduced, the heat evolution accelerated,



resulting in the explosion. Definitive experiments which support this sequence are described in the paper by Dartnell and Ventrone<sup>1</sup>.

#### ACKNOWLEDGMENT

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