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HEAT CAPACITIES AND PHASE TRANSITIONS OF OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE (HMX)

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ABSTRACT

The heat capacities and enthalpies of phase transitions of the four known polymorphs of HMX have been determined over the temperature range 320 to 530 K. All the measurements were done using a Perkin-Elmer DSC-1B differential scanning calorimeter coupled to a Digico Micro 16 computer which acted as a data logger. The stored DSC output was analysed by computer to determine the heat capacities. The results are compared with the literature values and analysed in terms of our solution enthalpy studies on HMX.

INTRODUCTION

Work has been in progress in our laboratories for several years on the determination of the crystal structures of a range of nitramines by X-ray diffraction techniques and recently much of the work has been concentrated on the structures of the various polymorphs of HMX[1]. It is in conjunction with these structural studies that the present thermodynamic studies were done. The determination of heat capacities by classical adiabatic calorimetry requires the use of elaborate and expensive equipment which we did not have available. Furthermore classical techniques require samples of several grams for a precise heat capacity study and in view of the explosive nature of HMX it could be dangerous to heat up several grams of HMX to its decomposition point.

The use of differential scanning calorimetry (DSC) for the determination of heat capacities has been known for several years[2] but the results obtained have been of variable quality due mainly to problems of thermal lag and to the high degree of non-linearity in the temperature calibration and baseline of the Perkin-Elmer DSC-1B instrument.

Richardson and this colleagues[3,4] have shown how these problems can be overcome so that reliable heat capacity data can be obtained by DSC which are within about two percent of the results obtained by classical adiabatic calorimetry. We have adopted the method developed by Richardson for our determination of the heat capacities of the four polymorphs of HMX.

EXPERIMENTAL

Materials

The HMX used throughout this work was a high purity sample (>99.9%) prepared and supplied by ERDE (Waltham Abbey). Details of the preparation of the various polymorphs of HMX have been given elsewhere[5].

The DSC machine was calibrated using the specific heat kit, supplied by Perkin-Elmer, consisting of discs of synthetic sapphire (aluminium oxide) with a calibration certificate based on the results of Ginnings and Furukawa[6]. A sample of high purity benzoic acid (Aldrich Gold Label, >99.9%) was used as a test substance to compare the results obtained by DSC with those obtained by conventional high-precision calorimetry.

Calibration of the DSC Machine

Only a broad outline of the calibration procedure will be given as the operation has been described by Richardson[3] in great detail. The first part of the calibration is

TABLE 1

Substance	*Melting point* $T(K)$	*Observed temp.* (K)	$\Delta T = (T - T_{obs})$
Gallium	303.0	293.7	9.3
Benzoic acid	395.2	393.1	2.1
Indium	429.6	429.1	0.5
Tin	505.1	506.4	−1.3
Lead	600.6	598.6	2.0
Zinc	692.7	682.9	9.8

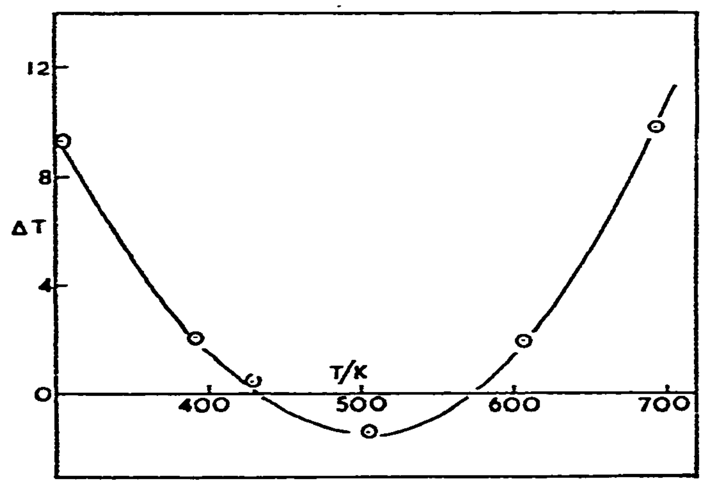

Fig. 1. Calibration curve for DSC head. $\Delta T = (T - T_{obs})$, vs. T.

to correct for differences between the dial temperature shown by the instrument and the true temperature at the DSC head. The temperature calibration is shown in Table 1 and Fig. 1.

The nominal scan speeds of 4 and 8 K min^{-1} were found to be 4.17 and 8.33 K min^{-1}, respectively. These were the only scan rates used.

It is unnecessary to calibrate the sensitivity of the DSC machine as this is taken into account by running a sapphire sample for every run on an unknown. Once the head had been calibrated it was used only for heat capacity work. All other correction factors for thermal lag, baseline non-linearity etc. are built into a computer programme which calculated the heat capacities from the DSC output.

Mode of operation

For each heat capacity determination three runs (empty pan, reference, sample) were done over 20°C intervals. The DSC output voltage was measured at one second intervals for each run and fed into a data logger (instead of a chart recorder) where it was stored on paper tape. The data were then analysed on a computer when all the various corrections were applied.

The size of the samples used varied between about 30 and 50 mg.

RESULTS AND DISCUSSION

After the DSC head had been calibrated, we tested the procedure by measuring the heat capacity of a highly purified sample of benzoic acid over the temperature range 260 to 350 K and compared the results with the literature values of Ginnings and Furukawa[6]. This comparison is shown in Fig. 2 where it can be seen that the agreement is excellent.

The heat capacities of the α, β, and γ forms of HMX were determined over the temperature range 320 to about 450 K when the β and γ forms undergo transition to the δ-form. Heat capacity measurements on the δ-form covered the temperature range from 320 to 520 K when decomposition begins.

The results are shown graphically in Figs. 3 to 6. Also shown (dotted lines) in these figures are the results obtained by Krien et al.[7]. The agreement between our results and those of Krien is quite good apart from the case of δ-HMX where there is a difference of about 70 J mol^{-1} K^{-1}. The transition enthalpies for the following changes were

α-HMX $\longrightarrow$ δ-HMX $T/\mathrm{K} = 470$

β-HMX $\longrightarrow$ δ-HMX $T/\mathrm{K} = 444$

γ-HMX $\longrightarrow$ δ-HMX $T/\mathrm{K} = 444$

also measured by DSC. The instrument was calibrated with a sample of high purity tin for the purpose of enthalpy calculations. The agreement between our results and those of Krien[7] and Hall[8] is again quite good (Table 2).

We have recently determined the relative stabilities of the four polymorphs of HMX at room temperature by solution calorimetry[5]. It is possible, therefore, by using Hess's law, to check the self-consistency of our DSC work on heat capacities and transition enthalpies with the transition enthalpies determined by solution calorimetry. This was done by setting up a thermochemical cycle of the form:

$$\begin{tikzcd}
\alpha\text{-HMX} \arrow[r] \arrow[d] & \delta\text{-HMX} \arrow[d] & T = 293\ \text{K} \\
\alpha\text{-HMX} \arrow[r] & \delta\text{-HMX} & T = 470\ \text{K}
\end{tikzcd}$$

By Hess's Law

$$\Delta H_{\alpha\to\delta}(293) = \Delta H_{\alpha\to\delta}(470) + \int_{293}^{470} (C_p(\alpha) - C_p(\delta))\,\mathrm{d}T$$

This type of cycle was evaluated for all three transitions $\alpha \to \delta$, $\beta \to \delta$, and $\gamma \to \delta$ using both our data and those of Krien et al. The results are shown in Table 3, where it can be seen that using Krien's value of C_p for δ-HMX leads to the result that δ-HMX is formed exothermically from the other three polymorphs at room temperature. This is contrary to our findings by solution calorimetry and also to the results reported by McCrone[9] on the solubility curves for the four polymorphs of HMX. The quantitative agreement between our DSC measurements and solution calorimetry results is not

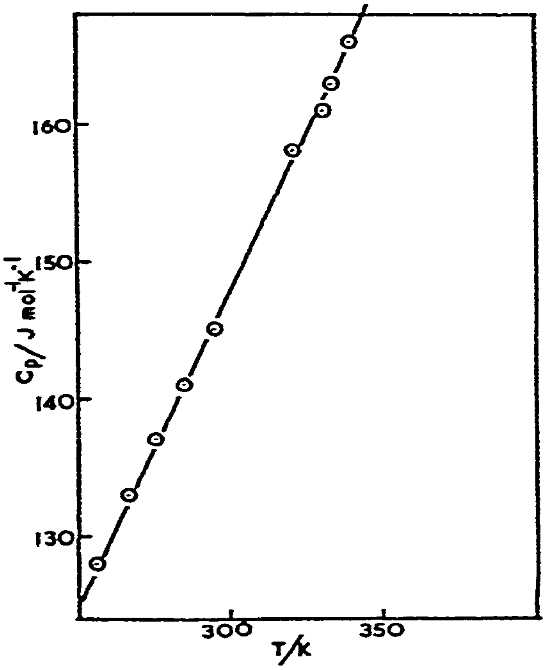

Fig. 2. Heat capacity of benzoic acid; O, this work; ——— from ref. 6.

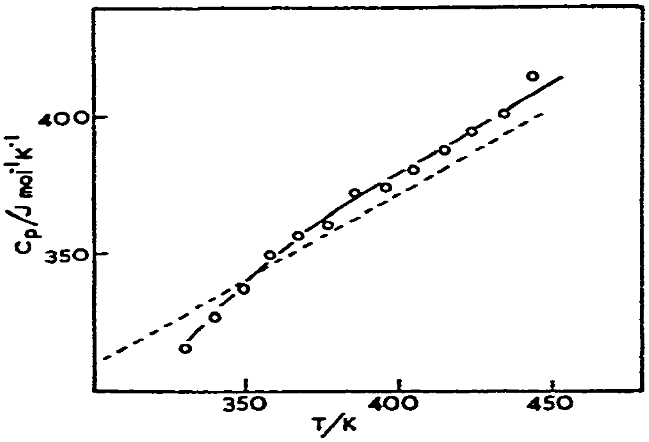

Fig. 3. Heat capacity of α-HMX; ○, this work; — — — from ref. 7.

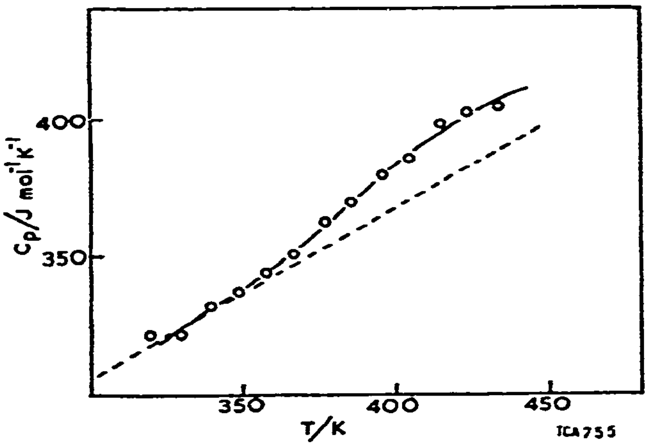

Fig. 4. Heat capacity of β-HMX; ○, this work; — — — from ref. 7.

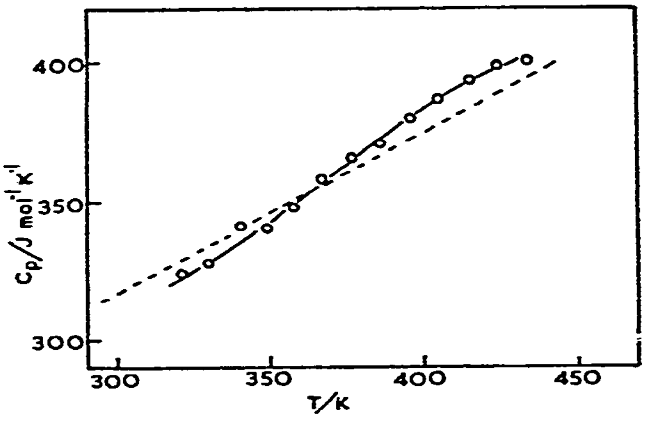

Fig. 5. Heat capacity of γ-HMX, ○, this work; — — — from ref. 7.

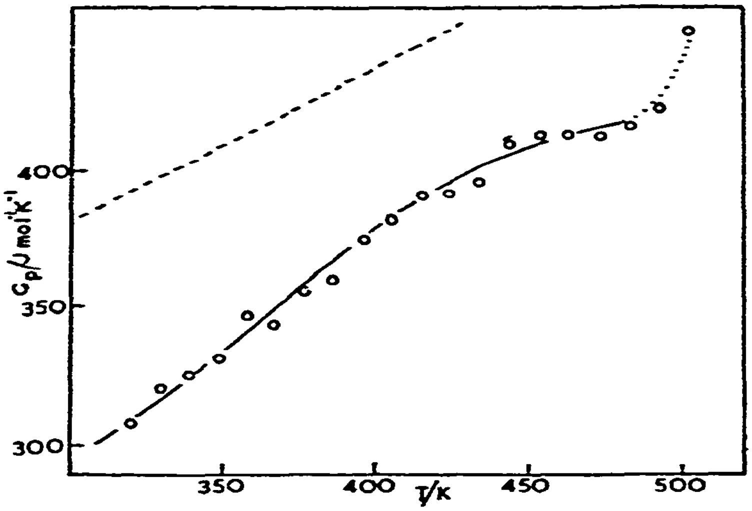

Fig. 6. Heat capacity of δ-HMX; ○ this work; — — — from ref. 7.

TABLE 2

HMX TRANSITION ENTHALPIES

T(K)	*Transition*	*ΔH_{trans} (kJ mol^{-1})*		
		This work	*Ref. 7*	*Ref. 8*
470	$\alpha \rightarrow \delta$	6.7	7.4	8.0
444	$\beta \rightarrow \delta$	9.3	9.8	9.6
444	$\gamma \rightarrow \delta$	2.7	2.8	—

TABLE 3

HMX TRANSITION ENTHALPIES AT 293 K

Transition	*ΔH_{trans} (kJ mol^{-1})*		
	This work	*Ref. 7*	*Solution calorimetry (ref. 5)*
$\alpha \rightarrow \delta$	7.3	−5.6	5.8
$\beta \rightarrow \delta$	10.3	−2.5	8.0
$\gamma \rightarrow \delta$	4.3	−7.1	2.6

particularly good but the order of stability, $\beta > \alpha > \gamma > \delta$ is the same by both methods and agrees with McCrone's results.

In conclusion, we believe that reliable and relatively accurate heat capacities can be measured by differential scanning calorimetry provided the necessary corrections are applied and that for substances which are potentially explosive, the method is safer than using a classical adiabatic calorimeter.

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REFERENCES

1 R. E. Cobbledick and R. W. H. Small, *Acta Crystallogr.*, B30 (1974) 1918.
2 M. J. O'Neill, *Anal. Chem.*, 38 (1966) 1331.
3 M. J. Richardson, *J. Polym. Sci.*, C38 (1972) 251.
4 M. J. Richardson and P. Burrington, *J. Therm. Anal.*, 6 (1974) 345.
5 J. Rylance, R. W. H. Small and D. Stubley, *J. Chem. Thermodyn.*, 6 (1974) 1103.
6 D. C. Ginnings and G. T. Furukawa, *J. Amer. Chem. Soc.*, 75 (1953) 522.
7 G. Krien, H. H. Licht and J. Zierath, *Thermochim. Acta*, 6 (1973) 465.
8 P. G. Hall, *Trans. Faraday Soc.*, 67 (1971) 556.
9 W. C. McCrone, in Fox, Labes and Weisberger (Eds.), *Physics and Chemistry of the Organic Solid State*, Vol. II, Interscience, 1965, p. 725.