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CHARACTERIZATION OF DMNB, A DETECTION AGENT FOR EXPLOSIVES, BY THERMAL ANALYSIS AND SOLID STATE NMR

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Abstract

The thermal properties of 2,3-dimethyl-2,3-dinitrobutane (DMNB), a detection agent for explosives, have been determined by DSC measurements. Additionally, the results of an NMR study are compared with conclusions arrived at in the literature with regard to the source of two endotherms observed in the DSC. The thermal decomposition of DMNB is characterized by an exotherm with an energy in excess of 3 kJ g^{-1}, observed in conjunction with a third endotherm resulting from the fusion of DMNB. Arrhenius parameters determined from both variable heating rate and isothermal measurements in the DSC are compared with predicted values assuming various mechanisms for the decomposition process.

Keywords: explosives

Introduction

The International Civil Aviation Organization (ICAO) is sponsoring an international project to develop methods for easily detecting explosives being transported in a concealed fashion. The ICAO has in place a Convention [1] specifying certain detection agents for incorporation into plastic explosives at the point of manufacture. These detection agents are ethylene glycol dinitrate (EGDN), 2,3-dimethyl-2,3-dinitrobutane (DMNB), and the nitrotoluenes, *o*-MNT and *p*-MNT. The volatility of these agents is the property used in their detection. The properties of the detection agents are compared in the preceding paper, which also describes the thermal properties of mixtures of the detection

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agents with the explosive, tetryl. In this paper, the results of an investigation of the properties of DMNB, the preferred detection agent, will be described.

Elias [2] has measured the vapour pressure of DMNB up to 323 K as well as its solubility between 278 and 308 K in ten solvents ranging in polarity from nonpolar (e.g. hexane) to polar (eg. DMSO). From these measurements, the enthalpies of sublimation and fusion have been estimated as 94±1 and 29±6 kJ mol^{-1}, respectively.

Thermocycling experiments on DMNB, with a DTA 'homemade device using a sealed glass receptacle', up to 410 K have detected two endotherms [3]. In the heating cycle, these endotherms occurred with onset temperatures of 322 and 388 K and transition energies of 1.0 and 23 kJ mol^{-1}, respectively. The first endotherm was described as a 'rotational transition', based on the results of dielectric constant measurements, which were invariant from 293 to 388 K. The second has been characterized as a crystalline transformation from triclinic to body centred cube from supporting X-ray evidence.

Earlier spectroscopic evidence [4] suggests that gauche rotamers predominate in the solid phase as a result of packing considerations i.e. intermolecular forces. In solution, a mixture of rotamers is believed to be present, with the transform predominating in nonpolar solvents and the gauche form increasing with increase in solvent polarity. From dipole moment measurements in CCl_4 solution the proportion of the rotamers has been determined and from this the internal energy difference between the rotamers was found to be 2.52 kJ mol^{-1}.

Independent studies of the thermal decomposition of DMNB in mesitylene solution at 488 K for a period of 3 h, have shown that the decomposition products are nitrous acid, a diene and an allylic nitro compound [5]. The expected products from a C–C bond cleavage reaction were not found. The authors suggest that nitrous acid is formed via a simultaneous pathway involving a five centred transition state rather than a two step process involving the homolytic cleavage of a C–N bond as the first step, followed by the subsequent loss of a β hydrogen. The composition of the products suggests that both single and double step elimination reactions occur.

We have conducted DSC and NMR measurements of the thermal properties of DMNB, the former up to and including the region of decomposition. This paper includes a detailed investigation of both the phase transitions and the kinetics of decomposition of DMNB.

Experimental

Material

2,3-dimethyl-2,3-dinitrobutane (DMNB) was acquired from Aldrich Chemical Co. and was stated to be at least 98 mol% pure. Samples of DMNB purified by sublimation or recrystallization showed no discernible difference in the DSC from those untreated.

Sample preparation

DSC measurements were conducted on standards and on DMNB loaded into sealed glass microampoules, similar to those described in the literature [6]. Glass capillary of 1.0±0.1 mm ID and wall thickness 0.35±0.05 mm (Kimble Products Inc.) was sealed at one end. The sample was compacted into the sealed capillary and the inner walls were carefully cleaned.

The microampoules containing sample were constructed by sealing the capillary with an oxyacetylene flame, while maintaining the end containing the sample at about 233 K by means of a specially designed holder cooled by a thermoelectric device. The microampoule could be manufactured in any size from 5 to 10 mm in length (limited by the size of the thermocouple platform in the DSC cell chamber).

For all the measurements done in this study, an effort was made to make the microampoules of uniform length and therefore of uniform volume, namely about 5 mm^3.

After sealing, each microampoule was examined under a microscope for any sign of a flawed seal or of premature decomposition of DMNB. The microampoule was reweighed to check for sample loss and/or decomposition. The microampoules were wrapped in silver foil, with a flattened side in contact with the platform. Consistency of results obtained for standard and DMNB analyses provides additional evidence for the integrity of the sealing technique. Some tests were also conducted using hermetic aluminium pans (with and without a pinhole) in a standard DSC cell and in a pressure cell (pan with a pinhole).

DSC measurements

A DSC 910-TA 2100 System (TA Instruments) with a carrier gas of dry oxygen-free nitrogen at a flow rate of 50 cm^3 min^{-1} was used. The instrument was calibrated with respect to temperature and heat flow using an appropriate pair from the standards mercury, water, gallium, indium, tin, zinc or lead. Calibration was checked by using another standard from the above list, with an intermediate melting temperature. Sample sizes of 2 mg and less than 1 mg were used, respectively, in the thermocycling and decomposition studies.

Heating and cooling rates of 5 K min^{-1} were generally used with the following exceptions: (i) in the thermocycling studies where 1 deg was also used and (ii) in the kinetic studies where heating rates from 2 to 10 K min^{-1} were used.

Isothermal kinetic results were analyzed using the Isothermal Kinetics package supplied by TA Instruments.

^{13}C *NMR spectra*

^{13}C NMR spectra were obtained at 45.26 MHz using ^{1}H cross-polarisation (CP) and decoupling, on a Bruker CXP 180 pulse spectrometer. One spectrum was obtained at room temperature using a Doty Scientific Inc. magic angle spinning (MAS) probe with a spinning rate of about 3.6 kHz. Static sample spectra were obtained at several temperatures using a Morris Instruments probe. Elevated temperatures were achieved using a stream of heated air and a Bruker BVT-1000 temperature controller.

^{13}C CP/MAS NMR spectroscopy [7] is routinely used to obtain high resolution spectra from solid samples. The transfer of ^{1}H polarisation to ^{13}C (CP) usually results in an enhanced signal and considerable savings in acquisition time. ^{1}H decoupling during signal acquisition removes the broadening effects of ^{1}H-^{13}C dipolar coupling, leaving the broadening due to the chemical shift anisotropy. This broadening and any residual dipolar coupling is removed by MAS.

Results and discussion

Phase transitions in DMNB

DMNB shows two endotherms below 400 K, in agreement with the published results [3]. The properties determined from these endotherms are listed in Table 1 and the thermogram is shown in Fig. 1. The results in Table 1 are independent of heating rates between 1 and 10 K min^{-1}. The onset temperatures of both transitions and the transition energy of the first transition are in close agreement with the earlier work. There is a substantial difference between the DSC derived energy and that reported previously [3] for the transition at 388 K. The low temperature endotherm is reported to be a result of an intramolecular transformation, in which there is rotation about the central C–C bond, resulting in a change from a molecule with NO_2 groups in the gauche position to one with these groups in the trans position. The energy change for the transition in the solid phase is smaller than that reported for the solution phase studies [4], despite indication that a significantly larger fraction of the DMNB is in the gauche form in the solid phase. It should be noted that the energy change observed in the microampoule experiments is a change in internal energy since these experiments are done at constant volume. The difference between ΔU and ΔH is within the estimate of the uncertainty in all cases. For the transition at 322 K, the n_2/n_1 value from

$$\Delta S = R\ \ln(n_2/n_1) \tag{1}$$

is 1.5±0.2 i.e. 3/2, within the experimental uncertainty. This value is similar to a range of values expected for an order – disorder process [8]. The thermal hysteresis for this transformation is illustrated in Fig. 2, where α is the fraction of the original DMNB transformed, determined by comparing the partial areas at each temperature to the total area of the peak in the thermogram.

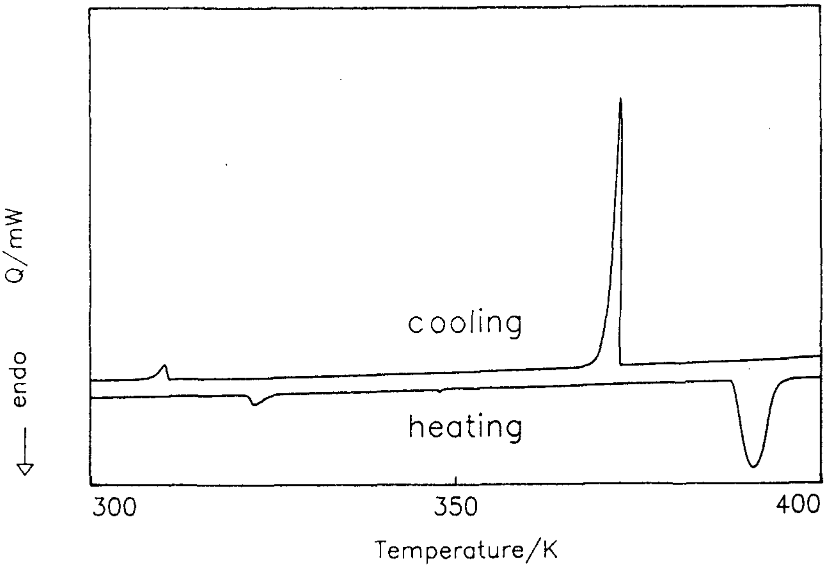

Fig. 1 Thermocycling of DMNB at 5 K min^{-1}

The ΔS value for the high temperature transition is the entropy change associated with the crystalline transition from a triclinic structure to a body centred cube. The thermal hysteresis for this transformation is shown in Fig. 3. The distortion in the curve in the cooling rate study is manifested in Fig. 4, where there is a deviation from the linear cooling rate. This is a result of the experimental conditions in which the backround cooling is compensated by instrumental heating to provide the net constant cooling rate. As the transition occurs, energy is supplied by the event and over compensation occurs, since there is no parallel decrease in the instrumental heating rate.

The room temperature CP/MAS spectrum (Fig. 5a) shows one resonance at 21.3 ppm for the four CH_3 carbons and another at 93.8 ppm for the quaternary

Table 1 Onset temperatures, T, ΔH, ΔS and hysteresis width for the solid-solid phase transitions of DMNB

Transition	T^*/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Hysteresis width/K
I → II	321±2	1.0±0.2	3.5±0.7	13±2
II → III	388±2	18.1±1.5	46.4±3.9	17±4

*heating cycle

carbons. Since there are no splittings of the lines it seemed unlikely that this type of spectrum would show any significant changes on heating through the two phase transitions. The room temperature static spectrum, however, revealed anisotropy of both lines (Fig. 5b), a property which could be different in the three phases.

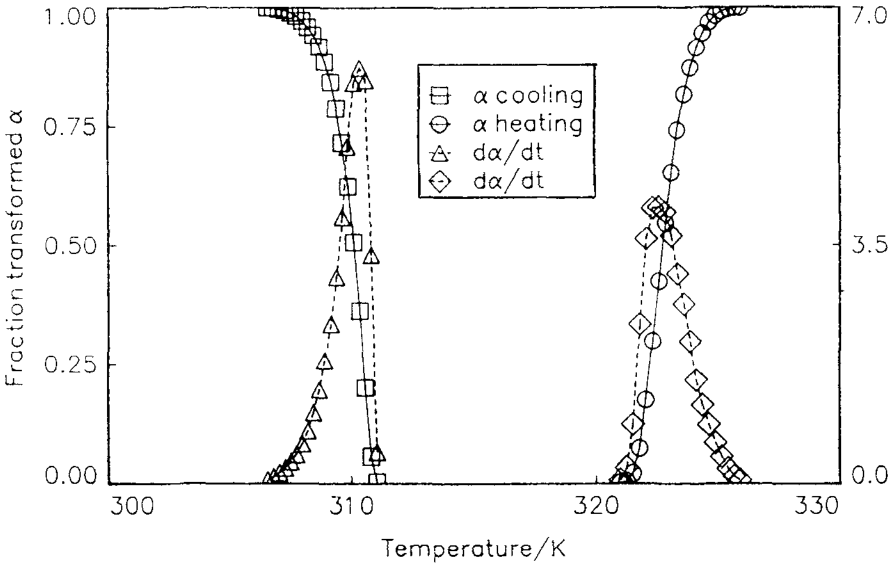

Fig. 2 Fraction of original DMNB transformed, α and dα/d*t* for the I to II transition

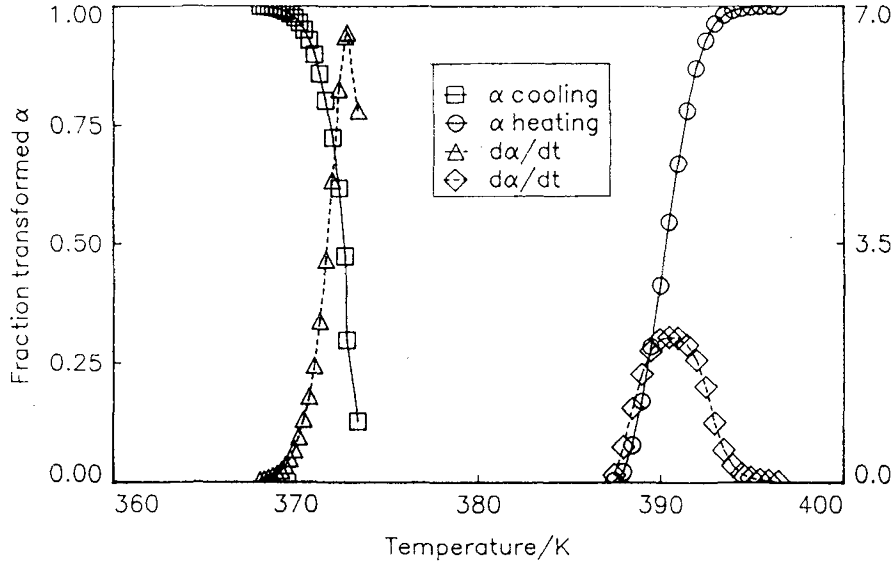

Fig. 3 Fraction of DMNB transformed, α and dα/d*t* for the II to III transition

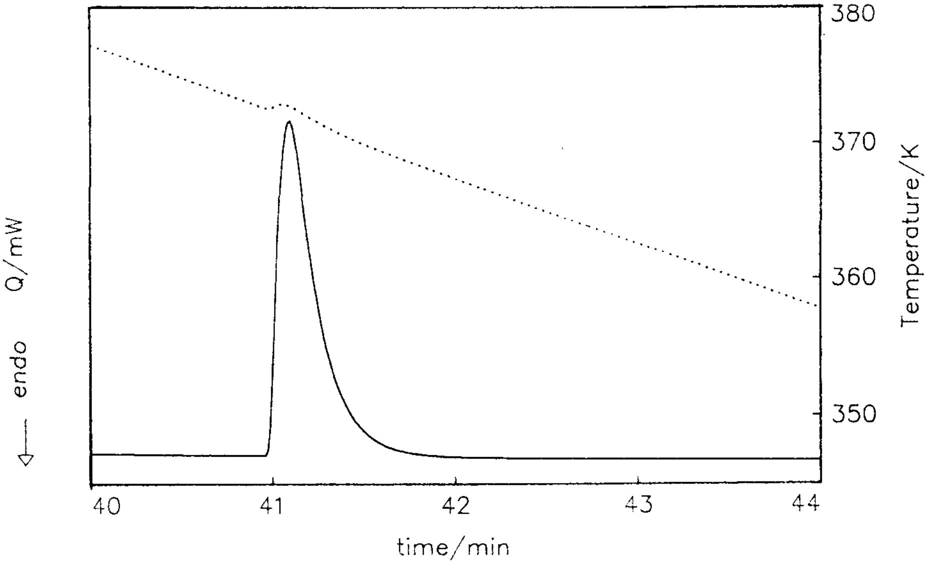

Fig. 4 Cooling of DMNB to illustrate break in constant cooling rate

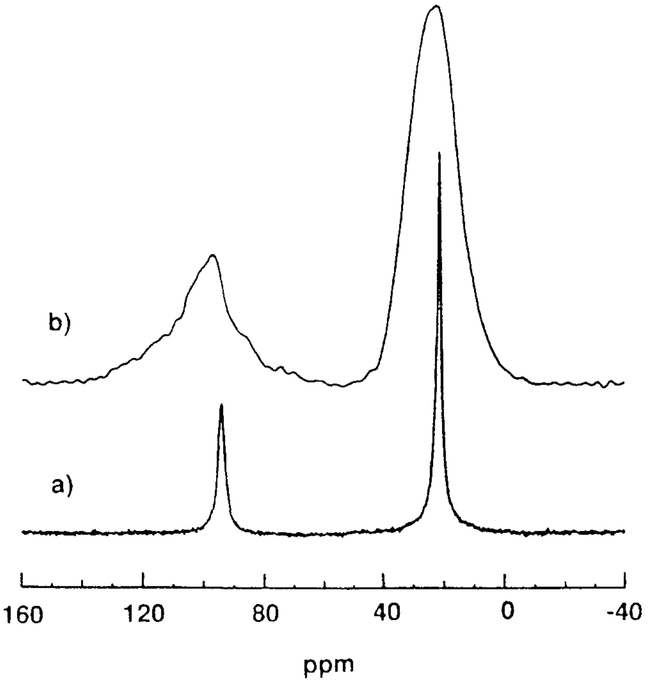

Fig. 5 Room temperature ^{13}C cross polarisation NMR spectra. a) with Magic Angle spinning at 3.6 kHz, and b) static

Static spectra at 306 and 318 K, just below the first transition, are basically identical to the room temperature spectrum (phase I) (Fig. 6a). Spectra in phase II display a narrower CH_3 line and a different shape for the quaternary carbon line (Fig. 6b). Changes in the anisotropy, and particularly the narrowing effects, are brought about by dynamic averaging of the chemical shift tensors. Thus there is a change in the dynamic state of the molecule in phase II, though it is not possible to be more specific about the nature of the motion. A much more dramatic change is observed in the phase III static spectra (Fig. 6c), the lines are very sharp and isotropic. This indicates a dynamic state which averages out all the residual anisotropy. In other words the molecules are rapidly reorienting, either among random orientations over a sphere or among several

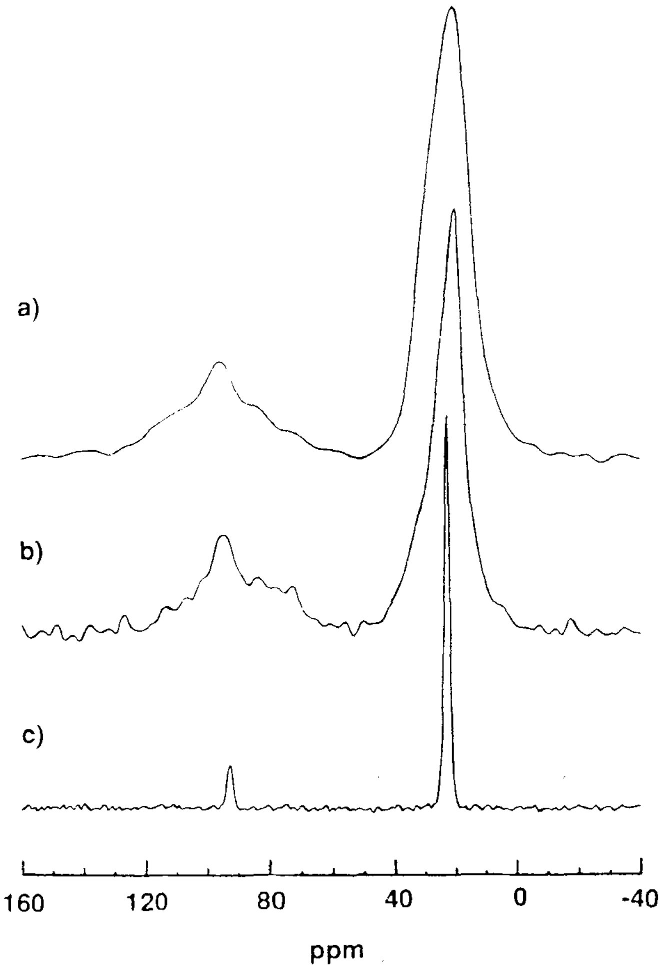

Fig. 6 Static ^{13}C CP NMR spectra of phases I, II and III at a) 318 K, b) 378 K and c) 398 K

sites with tetrahedral or cubic symmetry. This is the expected NMR behaviour for molecules in a plastic phase, and it is consistent with the crystallographic data which indicate a cubic structure for phase III (body centred cubic [3] or face centred cubic).

^{2}H NMR studies of a deuteriated sample would almost certainly yield much more specific information about the dynamics of the molecules in phase I and II.

Decomposition characteristics of DMNB

Figure 7 shows the exotherm characterizing the decomposition of DMNB in the microampoule at a heating rate, $\beta = 8$ K min^{-1}. This exotherm is preceded by an endotherm with an onset temperature of 475±2 K, in satisfactory agreement with the reported melting point of 480±5 K [9]. The exotherm could not be detected in hermetic pan experiments, either with or without a pinhole, due to the volatility of DMNB. Preliminary results indicate that the exotherm can be detected in pressure DSC measurements.

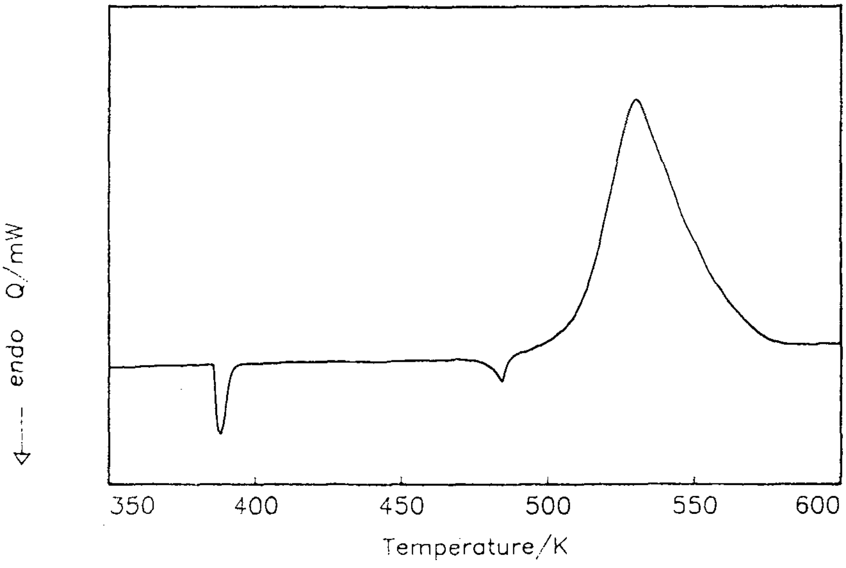

Fig. 7 Decomposition of DMNB at $\beta = 8$ K min^{-1}

The apparent peak temperatures and energy values of the fusion endotherm increase with increase in heating rate as illustrated in Table 2. This phenomenon is typical of substances that melt with decomposition [10]. Even so, the energy values do not reach either the $\Delta_{fus}H$ (298 K) of 14.9±3.4 kJ mol^{-1}, calculated from the enthalpies of formation of the solid and liquid [11] or the higher value estimated from the solubility measurements [2]. The source of the discrepancy between the DSC results and the calculated results is the overlap between the melting endotherm and the decomposition exotherm.

Table 2 Peak temperatures and apparent ΔH values for the crystalline phase transition, fusion and decomposition of DMNB at various heating rates, β

	Phase change		Fusion		Decomposition	
β/K min^{-1}	T^*/K	ΔH/kJ mol^{-1}	T/K	ΔH/kJ mol^{-1}	T/K	ΔH/kJ mol^{-1}
2.02	387	19.2	476	3.4	513	577
4.04	388	15.9	480	5.8	520	482
6.07	388	19.4	483	6.7	526	591
8.09	388	17.5	484	6.5	529	523
10.13	388	18.7	486	7.4	532	539
average		18.1±1.5				542±44

*onset

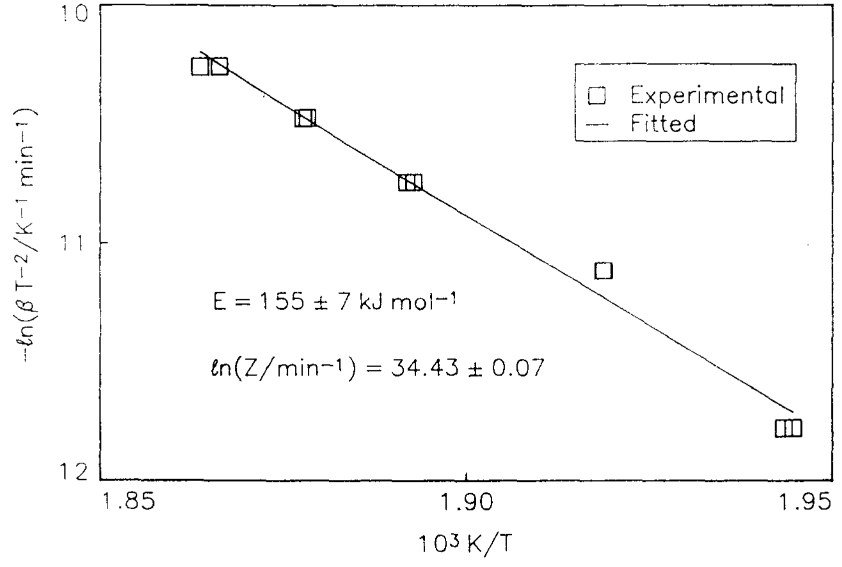

Fig. 8 Plot according to Eq. (3) to determine E and subsequently Z from Eq. (4)

The ΔH values for the decomposition process are independent of the heating rate. However, the asymmetric shape of the decomposition exotherm indicates that a complex process is occurring. The nature of the products obtained from the decomposition of DMNB in solution [5] also supports this conclusion. In spite of these observations and also the 'simultaneous' solid → liquid phase transformation, the Arrhenius equation

$$k = Ze^{-E/RT} \tag{2}$$

describing the dependence of k, the rate constant on temperature, T has been used to obtain the activation energy, E and the pre-exponential factor, Z from the following derived equations:

$$\ln(\beta/T_p^2) = \ln A - E/RT_p \tag{3}$$

where A is a constant, and

$$Z = \beta E e^{E/RT_p}/RT_p^2 \tag{4}$$

where T_p is the peak temperature. (Eqs (3) and (4) are only valid for a first order process.) The ASTM E 698 procedure [12] (Fig. 8) was used for this purpose and the results are recorded in Table 4. Isothermal aging tests at 493 K, in accordance with the above procedure, yielded ΔH values which agreed with those predicted from the Arrhenius parameters within ±10% and therefore meets the ASTM test of accuracy.

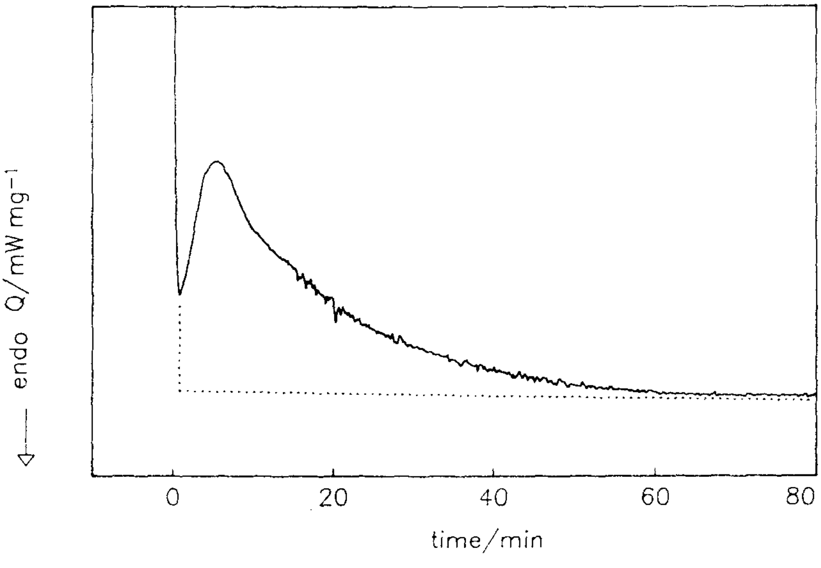

Fig. 9 Heat flow with time for DMNB at 502 K

Samples of DMNB were aged at 423 and 453 K for 65 and 16 h, respectively, quenched and subjected to a normal heating rate experiment at 5 K min^{-1}. The results indicated that approximately 10 and 70% of the original DMNB had reacted at the respective temperatures. It can be concluded that gas phase decomposition is a slow process and does not occur to any significant extent during the course of the DSC experiments.

A sample thermogram for the isothermal kinetics study is shown in Fig. 9. Experiments were conducted at the high end of the temperature scale to minimize the overlap between melting and decomposition. These results were analyzed in terms of both the nth order model

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{5}$$

and the autocatalytic model

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \tag{6}$$

where α is the fraction of DMNB decomposed. Figure 10 is typical of the data analysis obtained for the nth order model. In Table 3, the results obtained for each model are compiled. The simple n^{th} order model is statistically more significant than the autocatalytic model.

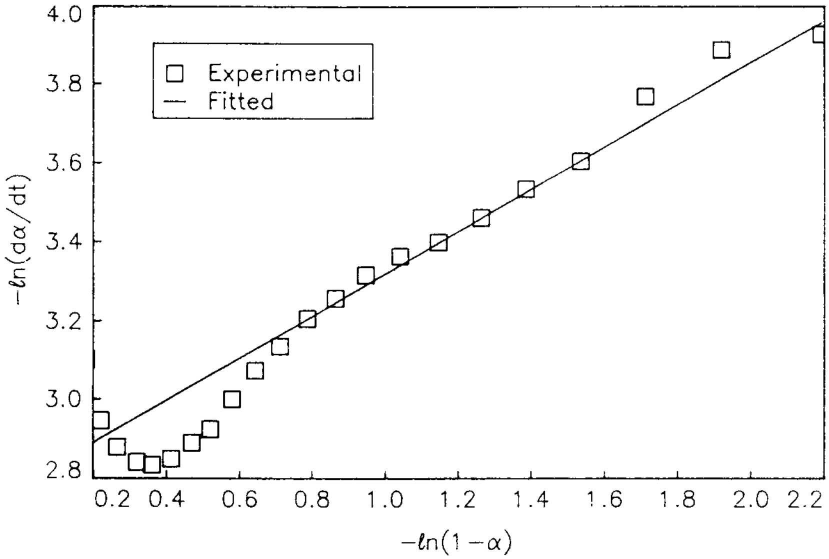

Fig. 10 Kinetic results for DMNB at 502 K according to Eq. (5)

The enhanced rate over that expected for a first order process may be a direct result of the increased pressure of DMNB in the ampoule, since there is a significant vapour pressure of DMNB at temperatures above 323 K (estimated to be about 3 bar at 423 K).

The Arrhenius kinetic parameters obtained from the ASTM method (1st order) and the isothermal kinetic study (n^{th} order) are compared with those pre-

Table 3 Rate constants and reaction orders *n* and *n* and *m*, respectively, for the n^{th} order and autocatalyc models

T/K	n^{th} order		Autocatalytic		
	n	10^2 k/min^{-1}	n	m	10^2 k/min^{-1}
492	0.534±0.065	3.00±0.19	0.65±0.11	0.108±0.089	3.63±0.61
497	0.565±0.076	4.22±0.32	0.81±0.12	0.185±0.092	5.9±1.0
502	0.574±0.073	6.21±0.47	0.86±0.13	0.180±0.093	8.6±1.6
507	0.574±0.082	9.77±0.81	0.69±0.14	0.15±0.12	12.6±2.7
Summary	0.557±0.075		0.73±0.12	0.147±0.095	

dicted [13] assuming either HONO elimination or C–N bond scission in Table 4. The HONO elimination model gives much better agreement with the experimental parameters than does the C–N bond scission model.

Table 4 Comparison of the Arrhenius kinetic parameters from the ASTM E 698 procedure [11] and the n^{th} order model with theoretical results for HONO elimination and C–N bond scission [12]

	ASTM	n^{th} order	HONO	C–N
E/kJ mol^{-1}	155±7	160±8	190.0	259.00
ln(Z/min^{-1})	34.43±0.07	35.5±2.1	30.5	44.39

Conclusions

DMNB undergoes two reversible phase transitions demonstrating large hysteresis and our DSC results are in essential agreement with earlier DTA measurements. The nature of these transitions i.e. gauche $\rightleftarrows$ trans and triclinic $\rightleftarrows$ bcc, is suggested by earlier work. Our NMR studies show that dramatic changes occur in the dynamic state of the molecule at these transitions and that the high temperature cubic phase is clearly a plastic crystal.

A successful technique for preparing microampoules of energetic material has enabled the first determination of the exotherm characterizing the decomposition of DMNB. The difference between the value from the DSC measurements and independent values for the heat of fusion of DMNB is due to the overlap of the fusion endotherm and the decomposition exotherm.

Similar Arrhenius parameters have been obtained from both the variable heating rate and isothermal kinetic studies, however the latter results suggest an overall order significantly less than unity. Comparison of these results with decomposition studies in solution and theoretical predictions from bond energy values indicates a similar decomposition mechanism to that described for the solution phase studies. This is supported by the occurrence of the fusion endotherm preceding but overlapping with the exotherm in the DSC measurements. Consequently, the necessity for liquid phase prior to decomposition is indicated.

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Zusammenfassung — Mittels DSC-Messungen wurden die thermischen Eigenschaften von 2,3-Dimethyl-2,3-Dinitrobutan (DMNB), einem Nachweismittel für Explosivstoffe ermittelt. In Ergänzung dazu wurden die Ergebnisse einer NMR-Untersuchung mit in der Literatur beschriebenen Schlußfolgerungen bezüglich des Ursprunges von zwei in der DSC beobachteten Endothermen verglichen. Die thermische Zersetzung von DMNB ist durch eine Exotherme mit einer Überschußenergie von 3 kJ g^{-1} gekennzeichnet, die in Verbindung mit der dritten Endothermen beobachtet wurde, die vom Schmelzen des DMNB herrührt. Die im DSC sowohl über eine unterschiedliche Aufheizgeschwindigkeit als auch über isotherme Messungen bestimmten Arrhenius'schen Parameter wurden mit vorausgesagten Werten verglichen, wobei für den Zersetzungsprozeß verschiedene Mechanismen angenommen wurden.