MEASUREMENT OF THE SENSITIZATION OF NITROCOMPOUNDS BY AMINES USING DIFFERENTIAL SCANNING CALORIMETRY

C. P. Constantinou and M. M. Chaudhri

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Abstract

We report a new method of making empirical measurements of the sensitization of nitrocompounds by amines based on thermal analysis. The method is sensitive, accurate and reproducible. We have used this method to measure the sensitization of nitromethane, N-methyl-N-(2,4,6-trinitrophenyl) nitramine (tetryl), picric acid and trinitrotoluene (*TNT*) by a number of aliphatic amines.

Introduction

Nitrocompounds are an important class of energetic materials. They are also known to be sensitized by amines through a chemical mechanism [1].

Nitromethane, the simplest nitrocompound, has been known since the 1940's to show increased sensitivity when mixed with amines. Quantitative measurements of the degree of sensitization* have been made by a number of workers. Engelke [2] measured a 43% decrease in the failure diameter** of nitromethane caused by the addition of 0.03% diethylenetriamine. Eyster in 1949 [2] and Cook and Haskins [3] used the gap test to demonstrate that the strength of the shock wave required to initiate a detonation in nitromethane is lowered substantially by the presence of eight different amines.

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* The term 'sensitization' is used in the explosives industry to mean 'increase in sensitivity'. There exist a number of industrial and laboratory tests for measuring the sensitivity of an energetic material to various stimuli (thermal, mechanical, electrical...)

** The failure diameter of an energetic material is the diameter of the smallest right circular cylinder in which it is possible to propagate a steady detonation wave.

Trinitrotoluene (*TNT*) and trinitrobenzene have also been demonstrated to be made more sensitive by amine additives. Cook and Haskins [4], for instance, used the Rotter dropweight impact test to show that the addition of amines makes these two aromatic polynitrocompounds more sensitive to low energy mechanical impact.

Large scale tests, such as the gap test or the Rotter drop-weight impact test, require substantial capital investments in the infrastructure before they can be undertaken. They also require the handling of large sample quantities which increases the risk of accidents.

During a comprehensive study of the thermal decomposition of nitrocompounds and nitrocompound–amine mixtures, we have developed a method for making physically meaningful measurements of the sensitization using much smaller sample masses than are generally used in industrial tests. This technique is sensitive, accurate and yields reproducible results.

In this paper we aim to demonstrate this method, which is based on thermal analysis and thus makes use of commercial laboratory equipment. In a previous publication [1] we presented our conclusions on the mechanism of sensitization, which we derived from a variety of experiments including thermal analysis.

Experimental methods

Solid nitrocompounds were obtained from Royal Armament Research and Development Establishment, UK. Spectrophotometric grade nitromethane and the amines diethylenetriamine (*DETA*), diethylamine (*DEA*), ethylenediamine (*EDA*) and n,n-dimethylethylamine (*DMEA*) were supplied by Aldrich Chemical Co. UK and specified as 99% pure. A 25% aqueous solution of ammonia was also supplied by Aldrich. The amines were purified by double distillation and were always used freshly distilled.

The instrument used for the thermochemical measurements was a Mettler TA3000. The temperature calibration was based on the melting points of indium (429.7 K), lead (600.5 K) and zinc (692.6 K). The energy calibration was carried out against the heat of fusion of indium (28.45 kJ·kg^{-1}). The exothermicity values reported are reproducible to within ±5%. The temperatures are reported within ±1 K.

Mixtures of nitromethane with the amines were prepared in air. Samples of nitromethane–*DETA* (10% by volume) were mixed in an argon atmosphere, with oxygen and water vapour levels restricted to below 6 ppm. These showed no significant mechanistic deviation from the samples mixed in air.

The remaining solid mixtures were also prepared in air by adding the amine to the solid aromatic nitrocompound and thoroughly grinding the mixture in a mortar and pestle into the form of a fine powder.

All nitrocompounds underwent a colour change when mixed with an amine. Samples of masses 2 to 10 mg were sealed in gold-plated stainless steel high pressure crucibles (Fisons Instruments, UK) under a mean pressure of 80 MPa using a specially designed hydraulic press. In this mass range no dependence was observed of the rate of reaction on sample mass. This implies that the kinetics of these reactions are not pressure-dependent under these conditions. The maximum capacity of one crucible was 50 μL. Such crucibles, when sealed, could contain pressure of up to 15 MPa. In all the experiments reported here, the sample crucible remained sealed throughout the duration of the reaction.

Results

Differential scanning calorimetry (DSC) provides a new technique for measuring the sensitization of nitrocompounds by amines. An example demonstrating the sensitization is presented in Fig. 1, which shows the DSC traces of pure nitromethane and a nitromethane-*DETA* (10% by volume) mixture taken at a heating rate of 10 deg·min⁻¹. The decomposition of the mixture, as indicated by the exotherm, begins at 453 K and the rate of decomposition peaks twice at 493 K and 538 K. On the other hand, nitromethane starts decomposing at 593 K and its rate of decomposition peaks at 688 K. The total amount of energy released during the decomposition, which is related to the area under the curve, can also be seen to increase substantially from 3000 kJ·kg⁻¹ in nitromethane to 4100 kJ·kg⁻¹ in the mixture. In the experiments reported here, nitromethane and nitromethane–amine mixtures decomposed in the liquid phase.

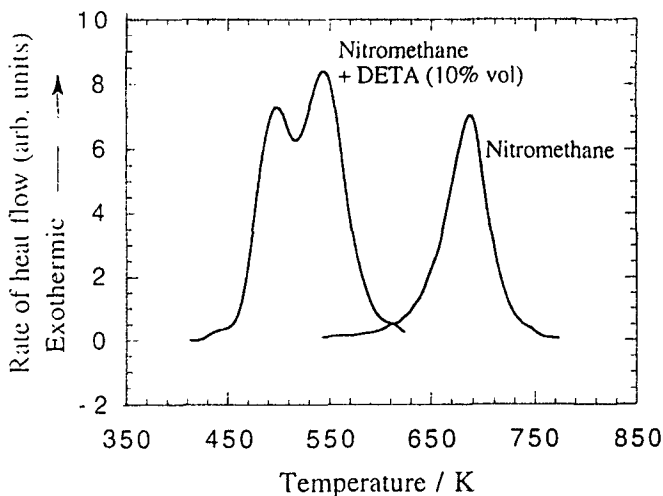Fig. 1 Dynamic DSC traces of nitromethane and a nitromethane-diethylenetriamine (*DETA*) (10% by volume) mixture taken at a heating rate of 10 deg·min⁻¹

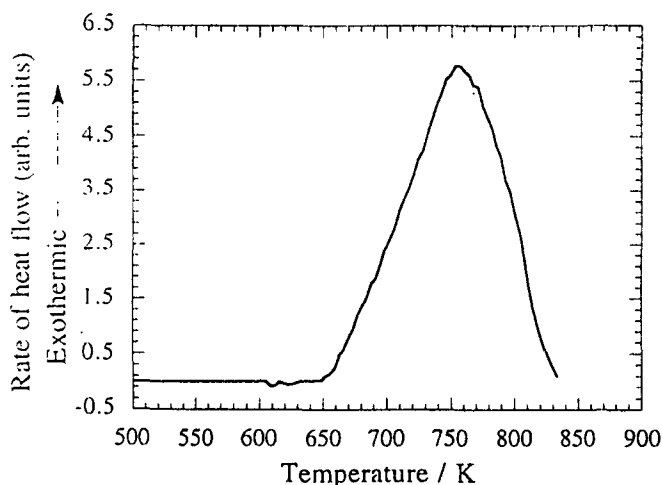**Fig. 2** Dynamic DSC trace of diethylenetriamine taken at a heating rate of 10 deg·min^{-1}

A similar dynamic experiment on the amine is shown in Fig. 2 *DETA* is found to start decomposing at 643 K. Its rate of decomposition peaks at 753 K and it has an exothermicity of 1300 kJ·kg^{-1} which is much lower than that of nitromethane. The exothermicities and decomposition temperatures of the various amines are shown in Table 1. All the amines decompose at substantially higher temperatures and have much lower exothermicities than nitromethane.

Table 1 The thermal decomposition parameters for various amines, as measured by dynamic DSC scans

Material	Onset of decomposition temperature/K	Peak decomposition temperature/K	Exothermicity/ kJ·kg^{-1}
Aqueous ammonia (25%)	613	635	1400
Ethylenediamine	673	764	830
Diethylenetriamine	643	753	1300
Diethylamine	613	710	1150
n,n-dimethylethylamine	660	749	1200

The sensitization of nitromethane by *DETA* is demonstrated in Fig. 1 by the drop in the decomposition temperature and the increase in the exothermicity. The two peaks in the dynamic DSC trace of the mixture constitute evidence that its decomposition takes place in two stages, each with its own rate-determining step.

Figure 3 shows the dynamic DSC traces of a series of nitromethane–DETA mixtures of varied amine concentration. All these scans were taken at a heating
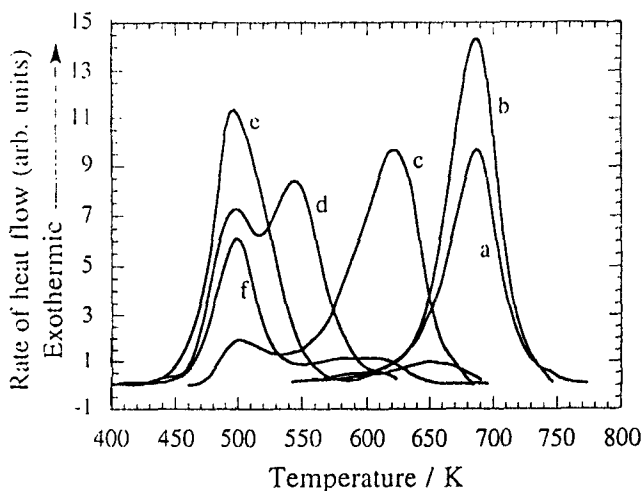
Fig. 3 The rate of release of thermal energy of various nitromethane –diethylenetriamine mixtures during a dynamic DSC scan at a heating rate of 10 deg·min^{-1}. The proportion by volume of amine relative to that of nitromethane is: a. 0%; b. 0.1%; c. 5%; d. 10%; e. 20%; f. 200%. The latter mixture contains equal molar fractions

rate of 10 deg·min^{-1}. Each of these mixtures showed sensitization as was manifest from an increase in the exothermicity or a decrease in the decomposition temperature. The exothermicity of these and other nitromethane–*DETA* mixtures is shown in Table 2. Two scans have been omitted from Fig. 3 for the sake of clarity. All mixtures of nitromethane with *DETA*, up to 50% by volume amine concentrations, have higher exothermicity than pure nitromethane. The maximum quantity of thermal energy was 4200 kJ·kg^{-1}, released by the 1% by volume amine mixture. This is substantially higher than the exothermicity of nitromethane (3000 kJ·kg^{-1}). All mixtures up to 20% by volume amine concentrations gave similar exothermicities, around 4100 kJ·kg^{-1}. It would seem that further increases in the amine concentration above 20% by volume bring about a dilution effect and a decrease in the exothermicity. A mixture with equal molar fractions was found to have an exothermicity of 2025 kJ·kg^{-1} whereas 5% by volume nitromethane in the amine gave 1300 kJ·kg^{-1}.

However, the drop in the decomposition temperature of nitromethane–amine mixtures is perhaps a more significant feature of Fig. 3. All the mixtures represented in Fig. 3 gave a double peak in their temperature variation of the rate of heat release; with the exception of the mixture containing 0.1% amine, all the first peak decomposition temperatures coincide at 493 K. The height of the first peak increases with amine concentration up to 20% by volume amine. In contrast, the maximum power during the second stage of decomposition decreases with amine concentration from 0.1 to 20% by volume. It also shifts from coin-

Table 2 The exothermicity of nitromethane-diethylenetriamine mixtures of varied amine concentration. (The relative percentage by volume of amine is indicated. The 200% mixture consists of equal molar fractions of the two components)

Sample	Exothermicity/kJ·kg^{-1}
Nitromethane	3000
Nitromethane + DETA(0.1%)	4150
Nitromethane + DETA(1%)	4200
Nitromethane + DETA(5%)	4100
Nitromethane + DETA(10%)	4100
Nitromethane + DETA(20%)	3900
Nitromethane + DETA(50%)	3200
Nitromethane + DETA(200%)	2025
Nitromethane + DETA(2000%)	1300

ciding with the peak rate of decomposition of pure nitromethane at 688 K gradually down to 544 K as one goes from the mixture with 0.1% by volume amine to that with 10% amine. It should also be noted that even though a dilution effect brings down the exothermicity of the mixture containing equal molar fractions, the first peak is still at 493 K and gives by far the higher rate of decomposition for that mixture.
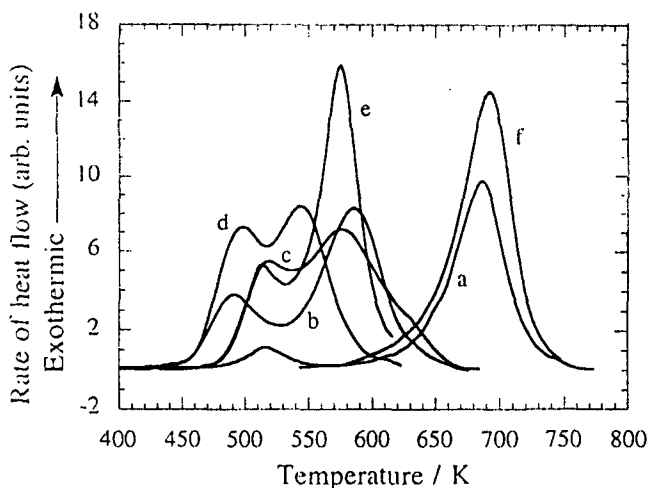

Fig. 4 Dynamic DSC traces at a heating rate of 10 deg·min^{-1}. a. nitromethane; b. nitromethane + ammonia (aq.); c. nitromethane + ethylenediamine; d. nitromethane + diethylenetriamine; e. nitromethane + diethylamine; f. nitromethane + n,n-dimethylethylamine. The concentration of each amine is 10% by volume and that of ammonia is 12.5% by volume

Figure 4 shows the dynamic DSC traces of a series of mixtures of nitromethane with different amines or ammonia. The nitromethane trace (curve a) is again given for comparison. The ammonia used was a 25% by weight solution in water. The decomposition of a nitromethane mixture with any of these amines can be seen to take place in two stages. The onset of decomposition and the first peak decomposition temperatures are not coincident for the different mixtures. The exothermicity also varies, depending on the amine present.

Table 3 The thermal decomposition parameters of nitrocompounds and nitrocompound – amine mixtures as determined by DSC. Peak decomposition temperatures refer to the first peak in the case of mixtures

Material	Exothermicity/ $kJ \cdot kg^{-1}$	Peak decomposition temperature/ K	Heat of explosion[5]/ $kJ \cdot kg^{-1}$
Nitromethane (NM)	3000	688	4544
NM+NH₃ (12.5% vol.)	4000	488	–
NM+EDA (10% vol.)	4231	518	–
NM+DETA (10% vol.)	4100	493	–
NM+DEA (10% vol.)	4700	513	–
NM+DMEA (10% vol.)	4750	518	–
TNT	3000	589	5066
TNT+DETA (10% wt.)	3000	458	–
Picric acid (PA)	2300	588	5025
PA+DETA (10% wt.)	3600	478	–
Tetryl	5100	585	5527
Tetryl+DETA (25% wt.)	2840	400	–

Table 3, which provides a summary of the DSC results, gives both exothermicity and first peak decomposition temperature values as obtained from these scans. Peak decomposition temperatures refer to the first peak in the case of the mixtures. For comparison, heat of explosion values are listed in the same table, wherever they were available.

Aqueous ammonia causes the highest drop in the temperature of onset of decomposition. The first peak occurs at 488 K as compared with the peak decomposition temperature of nitromethane which is given as 688 K. In contrast, *DMEA* gives the least sensitization. The first peak in the rate of decomposition of this mixture occurs at 518 K. It is also worth noting that all the mixtures have increased exothermicities as compared with pure nitromethane. The exothermicity for the nitromethane-aqueous ammonia mixture is quoted as measured,

with no allowance made for the presence of water. The exothermicity of a solution of gaseous ammonia in nitromethane would consequently be expected to be substantially higher.
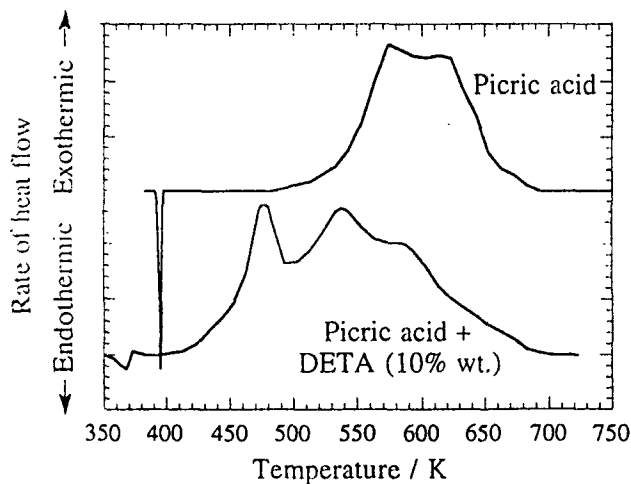

Fig. 5 Dynamic DSC traces of picric acid and a mixture of picric acid with *DETA* (10 wt%) at a heating rate of 10 deg·min^{-1}
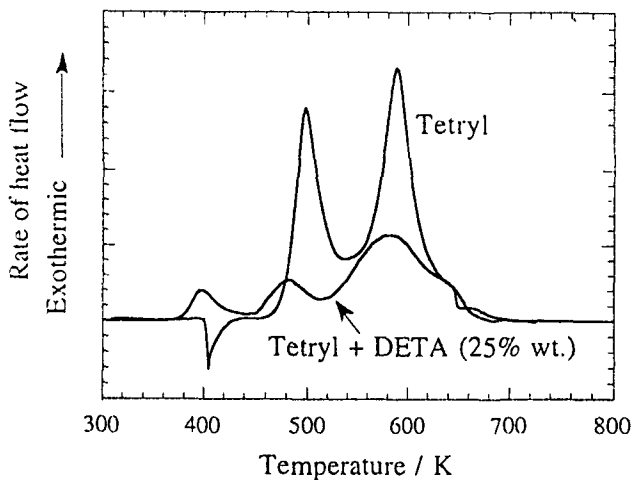

Fig. 6 Dynamic DSC traces of tetryl and a mixture of tetryl with *DETA* (10 wt%) at a heating rate of 10 deg·min^{-1}

Figures 5 to 7 show the dynamic DSC traces for pure picric acid, tetryl, *TNT* and mixtures of each of these with *DETA*. All the pure nitrocompounds were found to decompose in the liquid phase. The heat of fusion for each polynitro-
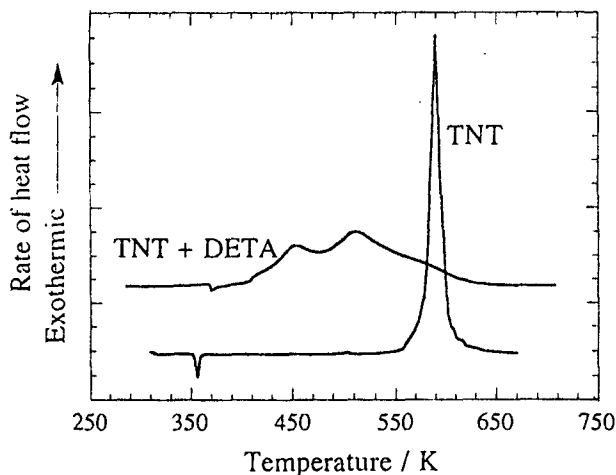
Fig. 7 Dynamic DSC traces of *TNT* and a mixture of *TNT* with *DETA* (10 wt%) at a heating rate of 10 deg·min^{-1}

compound, which was measured in this work as an accuracy test, is in good agreement with the value quoted in the literature (Table 4). In each case the decomposition of the mixture shows an additional reaction stage and starts at a lower temperature as compared to that of the pure nitrocompound. This is the case even with tetryl and picric acid, both of which show two-stage decomposition mechanisms in the pure form.

Table 4 Comparison between measured values for the heat of fusion of the solid nitrocompounds and values quoted in the literature

Material	Heat of fusion/kJ·kg^{-1}		Reference
	Measured value	Literature value	
Tetryl	80	80.0	5
Picric Acid	78	76.2	5
Trinitrotoluene	91	96.6	5

Picric acid starts decomposing at a temperature of 482 K. On the other hand, the decomposition of its mixture with *DETA* (10% by weight) starts at 400 K. The onset of decomposition temperature is correspondingly decreased by the presence of the amine, for tetryl from 455 K to 360 K and for *TNT* from 550 K to 405 K. All the mixtures examined show sensitization as indicated by the lowering of the peak decomposition temperatures. The exothermicity is increased by the presence of the amine in the case of picric acid from 2300 kJ·kg^{-1} to 3600 kJ·kg^{-1}, whereas for *TNT* it is found to remain unchanged

at 3000 kJ·kg^{-1}. For tetryl, it substantially decreased from 5100 kJ·kg^{-1} to 2840 kJ·kg^{-1}. The amine concentration in the tetryl–*DETA* mixture was 25% by weight. For the picric acid and *TNT* mixtures the amine concentration was 10% by weight.

Discussion

All the nitrocompound–*DETA* mixtures examined showed sensitization as indicated by the lowering of their onset of decomposition and peak decomposition temperatures as compared with those of the pure nitrocompound (Table 3). In addition mixtures of nitromethane with a range of amines or ammonia displayed increased exothermicity.

The peak decomposition temperature provides an easily measured gauge of the sensitivity of nitrocompounds. The changes involved in peak decomposition temperatures, when nitrocompounds are sensitized by amines, are sufficiently large to allow sensitive measurements. This is demonstrated by our measurements of the sensitivity of a series of nitromethane–*DETA* mixtures of varied amine concentrations. The sensitivity is shown to rise with concentration of *DETA* up to the 20% by volume mixture when a dilution effect sets in. This is consistent with previous measurements on the sensitization of nitromethane by DETA [3].

Thermal analysis equipment is commercially available at a resonable cost. When carefully calibrated, it enables temperature measurements, which are accurate to at least 1 K. The sample masses, are on the scale of mg; this substantially reduces the risks associated with working with energetic materials. Careful control of the cleanliness of the apparatus and frequent energy calibrations enable measurements with good reproducibility.

It should be emphasized that the peak decomposition temperature is only an empirical way of gauging the sensitivity of nitrocompounds. It lends it self as an empirical gauge because of the large changes caused by amines and the ease of the measurement. However, for a physically significant and more meaningful measurement of the sensitization, a careful kinetic analysis of the rate of decomposition of these materials is required. Such careful analyses using isothermal DSC data will be presented elsewhere.

Conclusions

We have demonstrated a technique, based on differential scanning calorimetry, of measuring the sensitization of nitrocompounds by amines. The method has been shown to have high sensitivity and accuracy. We have used this technique to show that different amines sensitize nitromethane to a different extent. We have also shown that the polynitrocompounds tetryl and picric acid

also undergo sensitization in the presence of amines, an effect similar to that previously demonstrated by *TNT* [4].

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References

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Zusammenfassung — Eine neue thermoanalytische Methode zur Durchführung empirischer Messungen an der durch Amine erfolgenden Sensibilisierung von Nitroverbindungen wird beschrieben. Die Methode weist eine hohe Empfindlichkeit, Genauigkeit und Reproduzierbarkeit auf. Anwendungsbeispiele zur Messung der durch eine Anzahl von aliphatischen Aminen erfolgenden Sensibilisierung von Nitromethan, N-Methyl-N-(2,4,6-trinitrophenyl)nitramin (Tetryl), Pikrinsäure und Trinitrotoluol (TNT) wurden gegeben.