HAZARD CHARACTERIZATION OF MIXTURES OF AMMONIUM NITRATE WITH THE SODIUM SALT OF DICHLOROISOCYANURIC ACID

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There has been recent interest in the hazard properties of mixtures of ammonium nitrate (AN) and the sodium salt of dichloroisocyanuric acid (SDIC) due to the possible involvement of such mixtures in the tragic accident in Toulouse, France, in September 2001. The thermal hazards of the mixtures were investigated using differential scanning calorimetry (DSC), accelerating rate calorimetry (ARC), thermogravimetry (TG), simultaneous TG-DTA-FTIR-MS, heat flow calorimetry (HFC), and isothermal nanocalorimetry (INC). The sensitivity of the mixtures to impact, friction, and electrostatic discharge was also investigated. ARC experiments on a 2 g mass of mixture in humid air revealed an onset temperature for thermal decomposition as low as 37°C. INC experiments revealed three overlapping exothermic peaks that resulted in a total energy release of 0.4 kJ g^{-1} over the course of thirteen days at 25°C. The reaction products were determined using simultaneous TG-DTA with FTIR and MS detectors, and they included CO_2, HCl, N_2, N_2O, NO_2 and Cl_2. The results from this study suggest that accidental mixing of bulk quantities of these materials would pose a considerable hazard and should be avoided.

Keywords: ammonium nitrate, chlorine, explosion, fertilizer, Grande Paroisse (AZF) fertilizer plant

Introduction

On September 21, 2001, about 300–400 tonnes of ammonium nitrate exploded at the Grande Paroisse (AZF) fertilizer plant in Toulouse, France. The explosion killed 31 people and injured over 2000. At present, the cause of the explosion is not known for certain. The internal investigation by Grande Paroisse's parent company, Atofina, has focused on three possible causes: scattering of metal fragments on the fertilizer storage facility by a plant explosion and subsequent detonation of fertilizers, anomalies in the power network, and contamination of ammonium nitrate (AN) by other chemicals produced at the site [1]. One of the other chemicals produced at the site is the sodium salt of dichloroisocyanurate (SDIC) [2], a chemical that is often used to disinfect swimming pools. Acceleration of the decomposition of AN due to compounds that contain chlorine is well known in the literature (e.g., [3]). Because the contamination of AN with SDIC is a possible cause of the explosion, there has been recent interest in hazard characterization of mixtures of these two substances.

In the present study, the thermal properties of AN and SDIC in a 50:50 mass% mixture were characterized using differential scanning calorimetry (DSC), accelerating rate calorimetry (ARC), thermogravimetry (TG), simultaneous DTA-TG- FTIR-MS, heat flow calorimetry (HFC), and isothermal nanocalorimetry (INC). The sensitivity of the mixture to impact, friction, and electrostatic discharge was determined using standard methods. The thermal properties of mixtures in other proportions (2:1 and 1:2) were studied by DSC, and the friction sensitivity of mixtures of various proportions was evaluated.

Experimental

Materials

A.C.S. reagent grade (98% purity) AN from Aldrich was used in the experiments. Unless otherwise stated, the AN was dried for 3 days at 80°C prior to use.

SDIC (98% purity) was obtained from Acros Organics. Unless otherwise stated, the SDIC was used as-received. When dry SDIC was used, the SDIC was dried for 3 days at 80°C.

Mixtures of AN and SDIC were prepared in small batches (200 mg total) prior to each experiment. To prepare 50:50 mixtures, approximately equal masses (100±2 mg) of AN and SDIC were weighed separately and were subsequently ground together with a mortar and pestle. The ground mixtures were then stirred with a spatula to improve the homogeneity of the mixture.

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Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed using a TA Instruments 2910 DSC. The DSC was purged with dry nitrogen gas at a flow rate of 50 cm^3 min^{-1}, and a heating rate of 5 K min^{-1} was used. The DSC was calibrated for heat flow and temperature using SRM standards indium, tin, and lead [4]. Sample materials were placed in hermetic aluminum pans, and an empty hermetic aluminum pan was used in the reference cell. For experiments on neat SDIC, approximately 5 mg samples were used. For experiments conducted on mixtures of AN and SDIC, 1–1.5 mg samples were used.

Accelerating Rate Calorimetry (ARC)

The apparatus used to conduct ARC experiments is a commercial adiabatic calorimeter that is used to assess the thermal hazard potential of energetic materials [5]. For each ARC experiment, 0.5–2 g of sample material were placed in a lightweight spherical titanium vessel, 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.

Experiments were started at ambient air pressure, and the standard ARC procedure of heat-wait-search was used. During this procedure, the temperature of the vessel was raised from an initial temperature in increments (the heat period) of 5°C for 0.5 g samples or 2°C for larger samples, and the vessel was maintained adiabatic during both a wait period (which allows for the dissipation of thermal transients) and a search period. 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 K min^{-1}. The temperature at which the self-heating rate first exceeded 0.02 K min^{-1} was recorded as the onset temperature. A 'true' onset temperature was obtained by extrapolating self-heating rate data to a value of zero.

The initial temperature for each heat-wait-search experiment was 30°C. The instrument terminated each experiment when any of the following criteria was met: a vessel temperature exceeding 350°C, a pressure exceeding 7 MPa, or a self-heating rate exceeding 5.0 K min^{-1} for 0.5 g samples or 1.0 K min^{-1} for larger samples.

In order to examine the effect of ambient moisture on the thermal stability of the mixture, four glass capillaries (~1.5 mm i.d. x 4.5 cm, sealed at one end) were each filled with about 90 µL distilled deionised water (~360 µL total) and were added to the ARC vessel before one of the heat-wait-search experi-

ments. The amount of water used was much more than the amount required to saturate the 10 mL of air in the ARC vessel at 60°C, but the air in contact with the sample may not have been saturated with water. The ARC vessel was connected to a pressure transducer by about 1 m of thin (0.76 mm i.d.) stainless steel tubing, and the tubing was located outside of the heated area of the ARC. The actual vapour pressure of water in the ARC vessel would have been some intermediate value between the vapour-pressure of water at the temperature of the vessel and the vapour-pressure of water in the line to the transducer. The open tops of the capillaries were in the neck of the vessel throughout the experiment, which allowed water to evaporate from the capillaries while keeping the sample out of direct contact with the liquid water.

Thermogravimetry (TG)

Thermogravimetry was performed using a TA Instruments 2950. Dry nitrogen gas was used to purge the system at a flow rate of 40 cm^3 min^{-1} to the balance and 60 cm^3 min^{-1} to the furnace. A heating rate of 5 K min^{-1} was used. For each experiment, approximately 5 mg of sample was placed on an open aluminum pan. The TA 2950 was calibrated for temperature, using a nickel Curie point technique [6], and for mass.

Simultaneous TG-DTA-FTIR-MS

A TA Instruments 5200 Thermal Analysis System with a 2960 simultaneous TG-DTA (SDT) module was used to characterize the mixture. Approximately 15 mg of sample material were placed in an alumina sample holder for each experiment, and a corresponding 15 mg mass of platinum foil was used as a reference material. The instrument was purged with dry air or helium at 50 cm^3 min^{-1}. In heating rate experiments, the sample and reference material were heated at a rate of 10 K min^{-1} from 25 to 200°C. Isothermal experiments were performed at 53, 58 and 70°C using helium as the purge gas.

TG mass, DTA baseline, and temperature calibration were performed prior to the experiments [4]. Temperature calibration was performed using SRM standard indium and high-purity aluminum wire. Note that the DTA was not calibrated for heat flow, so the DTA results should be interpreted as qualitative rather than quantitative measurements of enthalpy changes.

The SDT was interfaced to a Bomem MB100 Fourier Transform Infrared Spectrometer (FTIR) and a Balzers Thermostar GSD300 Quadrupole Mass Spectrometer (MS) to identify the evolved gases.

The FTIR interface consisted of a 5 mm i.d. Teflon® tube and a 10 cm Pyrex® cell with a 50 cm³ volume and KBr windows. A Whatman® QM-A quartz microfibre filter was placed at the FTIR inlet. The acquisition rate of the FTIR was one scan every minute and the time delay was about 10 s from the SDT furnace outlet to the FTIR cell. Bomem Grams/32 Version 4.04 software was used for data acquisition.

For the MS, a heated quartz capillary interface was placed near the sample pan in the SDT furnace. The temperature of the capillary interface was maintained at 150°C during the heating rate experiments and at 2°C above the temperature used during isothermal experiments. Data were acquired by Balzers Quadstar 422 version 5.04 software, which was programmed to acquire data using bargraph scan from 5 to 200 amu at a rate of 0.2 s/amu. The electron multiplier detector was set at 960 V, and the ion source was set to $9.6 \cdot 10^{-18}$ J (60 eV). The MS was calibrated for mass alignment and amplifier signal.

Heat Flow Calorimetry (HFC)

A Setaram C80 system was used to perform heat flow calorimetry. The C80 was connected to a custom manifold and high-pressure vessels, which are described elsewhere [7]. The C80 was calibrated for temperature using indium and tin. Approximately 180 mg of AN and SDIC mixture were placed in an alumina liner and loaded into a stainless steel high-pressure vessel. An equivalent mass of sapphire was loaded into the reference cell. The cells were purged three times with 1.4 MPa argon before each experiment, and experiments were conducted at ambient pressure of argon. The mixture was heated at 0.3 K min^{-1} from ambient temperature up to 190°C. This procedure was also performed on 0.8 g of AN, but the sample was only heated to 150°C.

Isothermal Nanocalorimetry (INC)

A Calorimetry Sciences Corporation model 4500 instrument was used to perform INC experiments on the AN and SDIC mixture at 20 and 25°C. The detector was calibrated at each temperature for heat flow using an internal electric heater, which was set to 100 μW. The accuracy of calorimetric data collected by the instrument was verified by conducting a standardized reaction experiment according to a protocol described elsewhere [8]. For each experiment, about 50 mg of sample was sealed in a 2 mL crimp-top glass vial with a natural rubber septum. An equivalent mass of alumina powder was sealed in a separate vial and placed in the reference cell.

Impact Sensitivity by BAM Fallhammer

The impact sensitivity of the AN and SDIC mixture was assessed using the standard BAM Fallhammer method [9]. The test involves the collision of a drop mass with an impact assembly that contains 40 mm³ of sample. The impact energy was controlled by the combination of drop mass and drop height used, and the allowable combinations are defined in the method. The limiting impact energy was recorded as the lowest energy at which a positive result, which is characterized by an audible report and/or deformation of the impact assembly, was obtained from at least one out of six repeated trials.

BAM Friction

Friction sensitivity measurements were performed on the AN and SDIC mixture using a standard BAM Friction test [10]. A friction load was selected by hanging a corresponding standard mass on the apparatus' loading arm. When the apparatus was activated, the loading arm brushed a porcelain peg against about 10 mm³ of sample that was loaded on a porcelain plate. The limiting friction load was recorded as the lowest energy at which a positive result, which is characterized by an audible report, crackling, sparking or a flame, was obtained from at least one out of six repeated trials.

Sensitivity to Electrostatic Discharge (ESD)

The electrostatic discharge sensitivity of the AN and SDIC mixture was measured using a procedure described elsewhere [11]. The procedure was first performed with sealed sample cells, and the entire procedure was repeated with open cells. The mixture was exposed to sparks with nominal energies of 6–156 mJ.

Results and discussion

Differential Scanning Calorimetry (DSC)

Typical DSC results for SDIC are shown in Fig. 1. For the as-received SDIC, the first exothermic peak occurs at 175–225°C and has an enthalpy change of 0.04–0.07 kJ g^{-1}, and the second exothermic peak occurs at 235–310°C and has an enthalpy change of 0.50–0.55 kJ g^{-1}. The presence of moisture in as-received SDIC is suggested by the endothermic peak that begins at about 100°C. This result is confirmed by DSC traces from experiments on dried SDIC, which do not exhibit any endothermic peaks near 100°C.

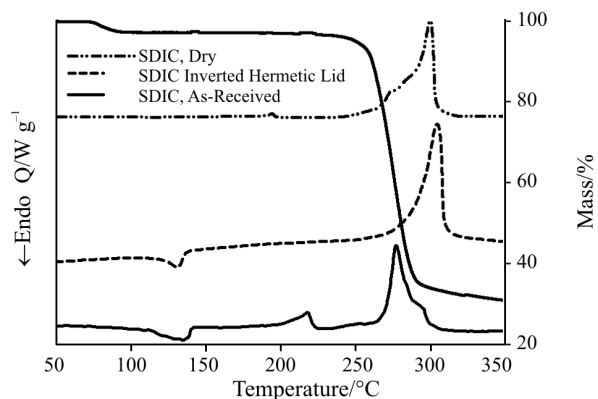Additional experiments on as-received SDIC were performed with the lid on the hermetic aluminum pan

Fig. 1 Typical DSC and TG results for SDIC. 5 mg samples, N_2 purge at 50 cm^3 min^{-1} (DSC) and 100 cm^3 min^{-1} (TG), and a heating rate of 5 K min^{-1}. DSC curves have been transposed for clarity
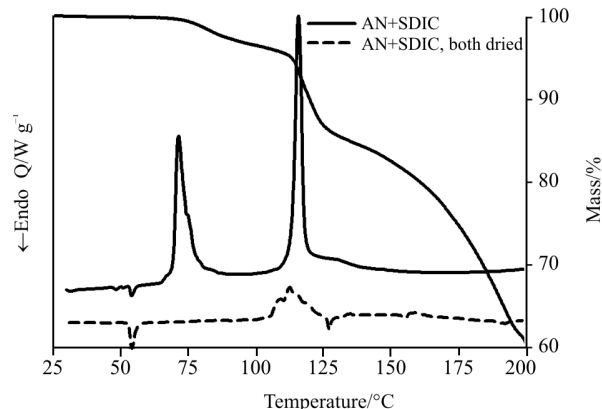

Fig. 2 Typical DSC and TG results obtained with a freshly prepared 50:50 mixture of AN and SDIC, and DSC results obtained with the mixture when AN and SDIC were both dried. 1–1.5 mg (DSC) and – 5 mg (TG) samples, N_2 purge at 50 cm^3 min^{-1} (DSC) and 100 cm^3 min^{-1} (TG), and a heating rate of 5 K min^{-1}. DSC curves have been transposed for clarity

inverted. Inverting the lid on the hermetic pan greatly reduced the headspace above the sample, and it was expected that this would reduce the amount of water vapour lost from the sample during the experiment. The first exothermic peak, which occurred at 175–225°C, was eliminated in the experiments where the lid was inverted and in the experiments on dried SDIC. These results suggest that the first exothermic peak is a result of an amorphous to crystalline phase transition that occurs after dehydration of the sample.

As can be seen in Fig. 1, DSC experiments on as-received SDIC do not show any exothermic activity below 175°C. AN is well characterized in the literature, and does not show any exothermic peaks below about 200°C [12]. In contrast, the DSC traces on the 50:50 mixture show an exotherm at about 60–90°C and a larger exotherm at 110–125°C. Typical DSC results for the mixture are shown in Fig. 2. The occurrence of exotherms in the mixture at temperatures well below those seen in the neat components indicates that the mixture is less thermally stable than its components. Also, the lack of endothermic peaks around 120 and 170°C, which correspond to AN's II–I phase transition and melting, respectively, suggests that most or all of the AN was consumed by the reaction.

DSC experiments were performed on the mixture to assess the repeatability of the results. A number of experiments were performed on mixtures that were prepared within a half an hour preceding the experiment, and the magnitude of their exotherms varied considerably: the first exotherm varied from 0.056–0.16 kJ g^{-1}, and the second exotherm varied from 0.085–0.19 kJ g^{-1}. Mass losses ranged from 20–40 %, indicating that gases escaped from the hermetic pans during the experiments. Nonetheless, the location of the exothermic peaks on the heat flow *vs.* temperature plots was repeatable to within about

±5°C. The variability may be due to poor homogeneity of the small (1–1.5 mg) samples and the lack of ambient humidity control during sample preparation.

A few of the mixtures were prepared several hours before testing on days when the ambient relative humidity was 70% or greater. These mixtures exhibited very small mass losses (~0.1%) and no measurable exothermic activity up to 200°C, even though experiments on fresher material clearly exhibited exotherms at lower temperatures. It appears that these samples reacted before being placed in the DSC, and the absorption of humidity from the ambient air may have accelerated the process. In order to examine the effect of humidity on the thermal stability of the mixture in more detail, DSC experiments were performed on 50:50 mixtures where both AN and SDIC were dried before mixing. An example is shown in Fig. 2. These experiments show minimal exothermic activity below about 100°C, which indicates that the absence of moisture increases the thermal stability of the mixture significantly.

Several DSC experiments were performed on mixtures which had either 2:1 or 1:2 mass ratios of AN to SDIC. Repeatability for these experiments was poor. The largest total enthalpy change of 0.8 kJ g^{-1} was observed for an experiment with a 1:2 ratio of AN:SDIC, which also exhibited the highest onset temperature, 90°C. All other experiments exhibited onset temperatures between 60–70°C, and total enthalpy changes ranged from 0.2–0.4 kJ g^{-1}. Nonetheless, the results showed that altering the ratio of the reactants did not measurably reduce the onset temperature of decomposition, nor did it conclusively increase the heat of reaction.

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Accelerating Rate Calorimetry (ARC)

Heat-wait-search ARC experiments in dry air were performed on 0.5 g of the mixture of AN and SDIC. The ARC-detected onset temperatures of thermal decomposition were 65 ±4°C, and the 'true' onset temperatures were about 1°C lower than the ARC-detected onset temperatures. Each initial exotherm occurred at a relatively slow rate and was followed by a faster exotherm.

The effect of sample size was explored by performing experiments with 1 and 2 g of sample. An experiment performed with 1 g of sample had an ARC-detected onset temperature of 49°C. With 2 g of sample, the ARC-detected onset temperature was further reduced to 40°C. Several experiments were performed with 2 g of sample in humid air, and an example of the observed self-heating rate *vs.* temperature profiles is illustrated in Fig. 3. These experiments yielded onset temperatures of 41±4°C. From the ARC results, it is not possible to conclude that humid air reduces the onset temperatures of the mixtures, but it is clear that increasing the sample mass reduced the observed onset temperatures considerably. This observation implies that the onset temperature of larger masses of mixture may be considerably lower than the onset temperatures reported here.
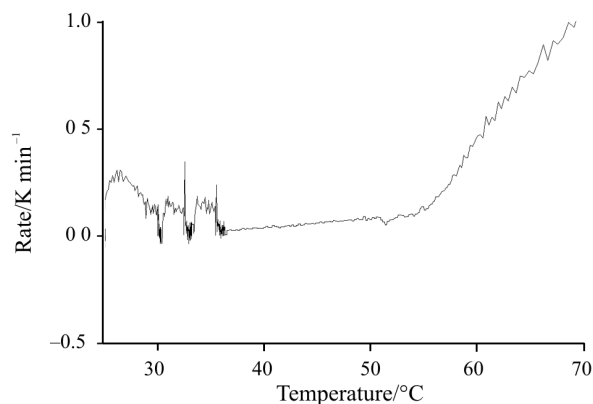

Fig. 3 Rate *vs.* temperature graph from a heat-wait-search ARC experiment performed on 2 g of a 50:50 mixture of AN and SDIC in humid air

Thermogravimetry (TG)

TG experiments were performed on as-received SDIC, and the results from a typical experiment are shown in Fig. 1. One small (~3%) mass loss step occurs between 70–100°C, which overlaps with a slight downward (i.e. endothermic) drift in the DSC curve and which is due to loss of water. This thermal event slightly precedes the corresponding event in the DSC, and the latter observation may be attributed to the open configuration and larger sample size used in the

TG experiments. No further mass loss was observed before 230°C, which is about the onset temperature of the second exotherm in the DSC. TG experiments performed on dry SDIC exhibit mass loss curves that are nearly identical to the curves for as-received SDIC, but they lack the mass loss step between 70–100°C.

TG experiments were also performed on the mixture of dry AN and as-received SDIC, and the results from one experiment are shown in Fig. 2. During the experiments, one small (~3%) mass loss step was observed between 65–95°C, while a larger (7–12%) mass loss step was observed between 100–135°C. The derivative peaks of these two mass loss steps occurred at approximately 82 and 120°C. These two mass loss steps occur in similar temperature ranges to the exothermic peaks observed in the DSC, which suggests that an exothermic reaction with gaseous products occurs during these mass loss steps. Additional mass loss occurs above 135°C, but no corresponding peaks were observed in the DSC curves. The latter observation may be due to the open and closed sample holder configurations employed in the TG and DSC experiments, respectively.

TG experiments were performed on 50:50 mixtures where both AN and SDIC were dried before mixing. The mass loss curves are similar to those discussed above, but they lack the 3% mass loss step between 65–95°C. The 3% mass loss step can be correlated with the first exotherm in the DSC, which would suggest that the presence of water accelerates the reaction. Nonetheless, part of the mass loss is most likely due to endothermic evaporation of water from the SDIC.

Simultaneous TG-DTA-FTIR-MS

The TG-DTA (SDT), FTIR, and MS data from experiments on SDIC in helium and air are shown in Figs 4 and 5, respectively. In Figs 4a and 5a, each TG curve shows a small (~2.5%), endothermic mass loss step between 75–125°C. These results are similar to those obtained by TG, but they are shifted to slightly higher temperatures due to the higher heating rate used in the SDT (10 K min^{-1} *vs.* 5°C min^{-1}). The FTIR results are shown in Figs 4b and 5b, and the MS results are shown in Figs 4c and 5c. Only H_2O and traces of both N_2O and CO_2 were identified as evolved gases. The presence of air did not appear to accelerate decomposition.

The detailed TG-DTA results from experiments on the mixture in helium and air are shown in Table 1. In Fig. 6a, the TG curve in helium exhibits three mass loss steps: one small (~3%) mass loss step between 68–110°C, a larger (~14%) overlapping mass loss step between 110–135°C, and a third mass loss step
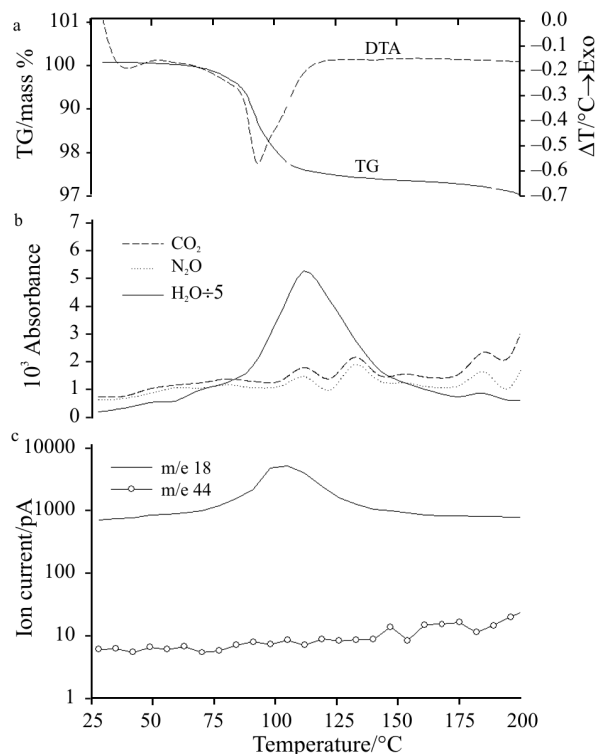
Fig. 4 SDT experiment on SDIC in inert gas. 15 mg sample, He purge at 50 cm³ min⁻¹, and a heating rate of 5 K min⁻¹
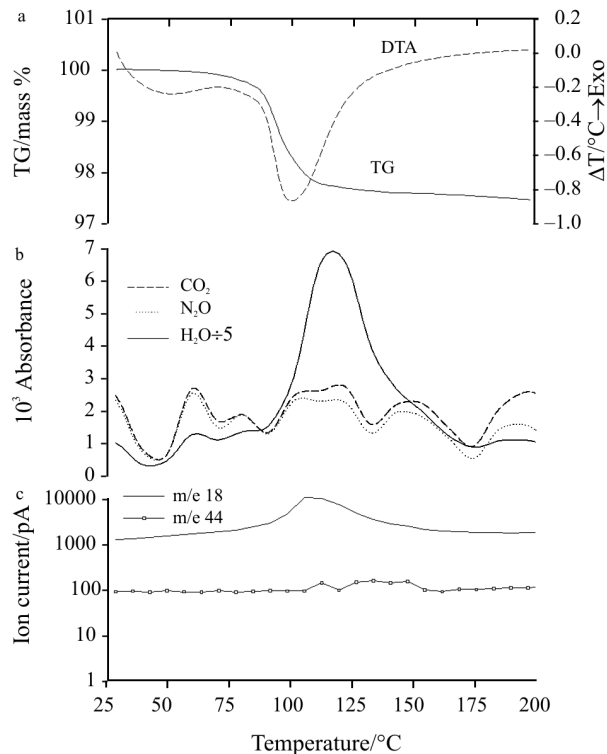

Fig. 5 SDT experiment on SDIC in air. 15 mg sample, air purge at 50 cm³ min⁻¹, and a heating rate of 5 K min⁻¹

that starts at about 135°C and continues until the end of the experiment (200°C). The TG results in air, shown in Fig. 7a, exhibit a very different second mass loss step, which is considerably larger (~28% *vs*. 14%) and more exothermic than the corresponding step in helium. The third mass loss step is smaller in air than in helium.

The FTIR data for the experiments on the mixture in helium and in air are shown in Figs 6b and 7b respectively. As was the case with SDIC, only H_2O, N_2O and CO_2 were identified as evolved gases.

The MS detected the evolution of several other species from the mixture, and these results are shown in Figs 6c and 7c. In helium, the evolution of N_2 (*m/e* 28), NO (*m/e* 30), HCl (*m/e* 36), NO_2 (*m/e* 46), and Cl_2 (*m/e* 70) were detected in addition to the H_2O (*m/e* 18), CO_2 (*m/e* 44) and N_2O (*m/e* 44) detected in the FTIR. Note that species with *m/e* 72 and 74, which are due to isotopes of Cl_2, were detected in the MS but were omitted from the figures for the sake of clarity.

In air, many of the same products were detected in the MS. Notably, however, no NO was detected, which is likely due to oxidation of this product with the oxygen available from the air. The evolution of N_2 was not detected, but the high N_2 levels in air likely obscured its evolution. Products with *m/e* of 49, 51, 52, and 53 were also detected, but only *m/e* 51 is shown in Fig. 7c for clarity. These unidentified products evolved with a nearly identical trend as mass
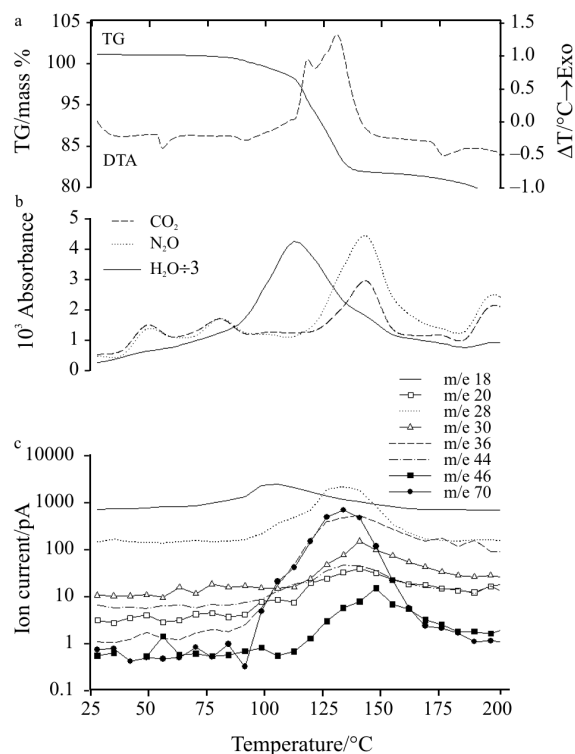

Fig. 6 SDT experiment on a 50:50 mixture of AN and SDIC in inert gas. 15 mg sample, He purge at 50 cm³ min⁻¹, and a heating rate of 5 K min⁻¹

**Table 1** Summary of TG-DTA results for the mixture of AN and SDIC

Atmosphere	T_o[a]/°C	T_p[b]/°C	A_p[c] /K min mg^{-1}	Δm_1[d]/%	Δm_2[e]/%	Δm_3[f]/%
Helium	68	131	0.51	3.1	13.7	4.5
Air	75	131	0.21	2.6	27.7	1.4

[a] T_o is the temperature at which a deflection from the baseline in the TG curve is observed; [b] T_p is the temperature at which the maximum temperature difference is observed in the DTA curve; [c] A_p, the area under that DTA peak, can be correlated with ΔH and is useful for qualitative comparisons; [d] Δm_1 is the mass loss between 68–10°C; [e] Δm_2 is the mass loss between 110–135°C; [f] Δm_3 is the mass loss between 135–200°C

51, albeit with varying intensities. The products may all be fragments resulting from ionization of H_2NCl (m/e 51), with mass 53 possibly being H_2NCl with a mass 37 isotope of chlorine. The evolution of mass 64, possibly C_2H_5Cl, was also detected in air.

It has been suggested that small quantities of nitrogen trichloride (NCl_3), a very reactive substance, may be produced during the decomposition of the mixture. Contact of chlorine with ammonium salts, above 0°C, is known to produce the highly explosive product NCl_3 [13]. Pure NCl_3 has a boiling point of 71°C [14], and the liquid has been reported to explode on heating to 60 or 95°C [13]. Isothermal SDT experiments at 53, 58 and 70°C were performed in an attempt to produce NCl_3, while avoiding its decomposition. No gas evolution was detected by FTIR and MS in any of the isothermal experiments (despite mass losses of 2–6 % over 24 h), which implies that little or

no chlorine gas was produced during these experiments. As a result, little or no NCl_3 formation would be expected. The conditions in the SDT (i.e., the sample being in an open container with the product gases continuously removed by purge gas) may not have been conducive to the formation of NCl_3. Even if some NCl_3 had been produced, it may have decomposed before reaching the detectors, despite the precautions, since the decomposition of NCl_3 is a spontaneous reaction:

$$NCl_3(l) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}Cl_2(g), \qquad (1)$$
$$\Delta H = -230\,\text{kJ mol}^{-1}\ NCl_3 \quad [13]$$
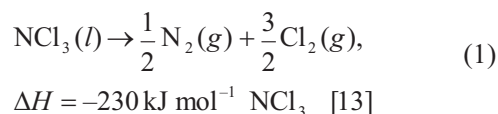
Note that both N_2 and Cl_2 were detected by MS in the heating rate study on the mixture in helium, as shown in Fig. 6c. In addition, the presence of background levels of CO_2 would have masked any NCl_3 peaks in the FTIR (as reported in [15]).
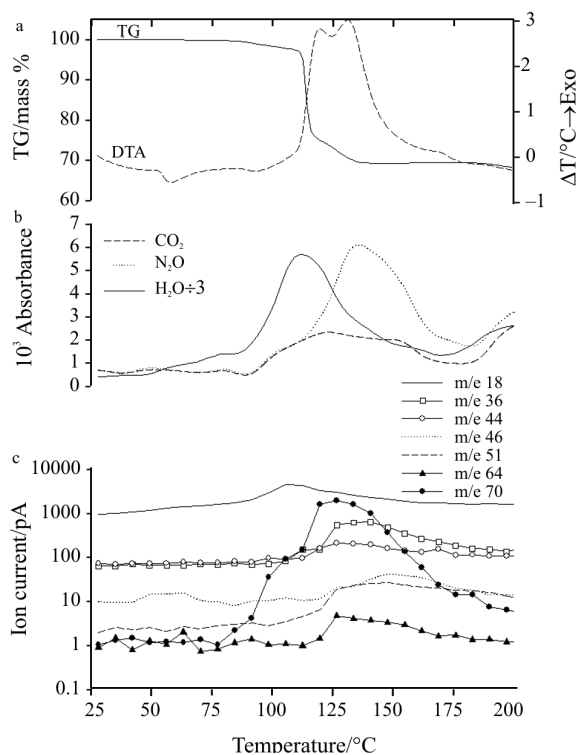
Heat Flow Calorimetry (HFC)

Data from HFC experiments are shown in Fig. 8. The heat flow *vs.* temperature curve for the AN and SDIC mixture is similar to that obtained in the DSC, but the HFC data exhibit exotherms about 5–10°C below the DSC results. The differences can be attributed to the
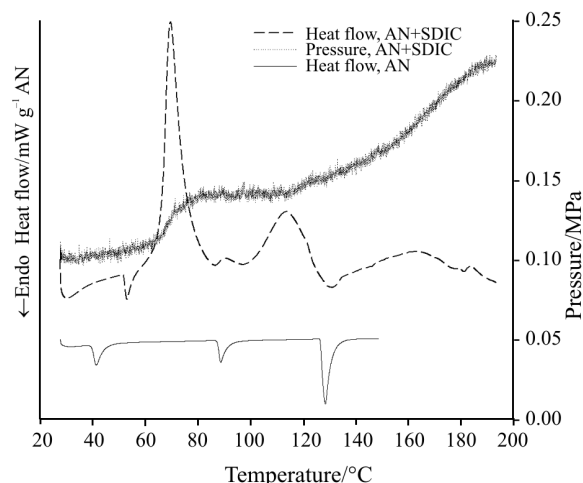

Fig. 7 SDT experiment on a 50:50 mixture of AN and SDIC in air. 15 mg sample, air purge at 50 cm^3 min^{-1}, and a heating rate of 5 K min^{-1}

Fig. 8 HFC experiment on 0.8 g neat AN and 180 mg of a 50:50 mixture of AN and SDIC in argon. Heat flow curves have been transposed for clarity

lower heating rate and large sample size used in the HFC. The upward slant on the baseline at the beginning of the run suggests that an exothermic reaction begins almost immediately. This observation is supported by the INC results, discussed below. As shown in the Figure, AN exhibits three endothermic phase transitions (IV to III, III to II, and II to I) between room temperature and 150°C, and no measurable exothermic behaviour.

Due to the absence of a clear baseline for the mixture, it is difficult to quantify the magnitude of the observed exotherms to a high degree of precision. A conservative estimate of the magnitude of the first exotherm is 0.27 kJ g^{-1}. This value is considerably larger than the one that was obtained in the DSC, and this discrepancy may be due to the larger and more representative sample size used in the HFC. The magnitude of the second exotherm was estimated to be 0.14 kJ g^{-1}, which is within the range obtained in the DSC.

Isothermal Nanocalorimetry (INC)

The heat flow *vs.* time data from INC experiments at 20 and 25°C on the AN and SDIC mixture are shown in Fig. 9. The data from the first few hours should be ignored because the large signal is caused by the sample vial coming to thermal equilibrium with the calorimeter. As shown in Fig. 9, at 25°C, three overlapping exothermic peaks are observed over a thirteen-day period. The initial exothermic peak is the smallest, but its presence indicates that a measurable reaction begins almost immediately. The second exothermic peak is the largest, and its occurrence may be due to additional reactions involving the products of the reaction associated with the first exothermic peak. Because the peaks overlap to such a large extent, it is not possible to quantify the energy release for each individual exothermic peak. The total energy
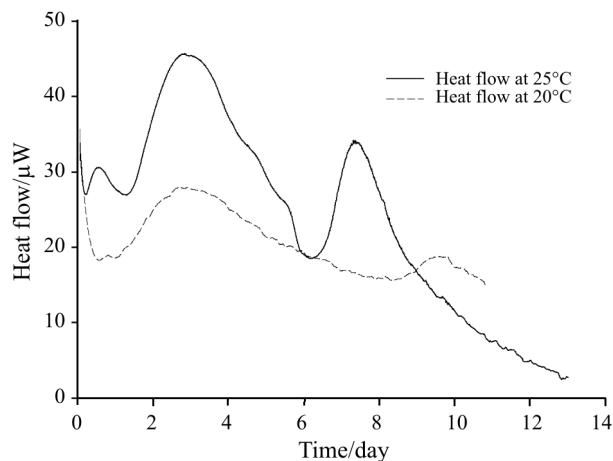
release was found to be 0.4 kJ g^{-1}, which is consistent with the HFC results. For comparison, the molecular explosive PETN produces 4 kJ g^{-1} during decomposition [16], which is an order of magnitude greater than the mixture. Nonetheless, the mixture is hazardous because it is unstable at room temperature, whereas PETN is relatively stable below its melting point (~138°C [7]).

At 20°C the first exothermic peak is almost completely obscured by the second peak. The second and third exothermic peaks were much broader than those at 25°C, which indicates that the reaction rate is considerably lower at 20°C. Nonetheless, the experiments show that the reaction proceeds at a measurable rate even below room temperature.

Impact Sensitivity by BAM Fallhammer

The limiting impact energy of the mixture of AN and SDIC was found to be 7.5 J. For comparison, the secondary explosives PETN and RDX have limiting impact energies of 3 and 5 J respectively [9]. Under the UN guidelines for Transport of Dangerous Goods (TDG), substances that exhibit a limiting impact energy of 2 J or less are considered too sensitive for transportation in bulk quantities. Thus, although the mixture is not exceptionally sensitive to impact, a result of 7.5 J indicates that the mixture can be initiated by impact.

BAM Friction

The limiting friction load of various mixtures of AN and SDIC is shown in Table 2. For comparison, the secondary explosives PETN, RDX and TNT have limiting loads of 80, 120, and 360 N respectively [10]. Under the UN guidelines for TDG, substances that exhibit a limiting load of less than 80 N are considered too sensitive for transportation in bulk quantities. Thus, none of the mixtures are exceptionally friction sensitive, but the probability of initiating their energetic decomposition is relatively high when subjected to large friction loads. Neither increasing nor de-

Fig. 9 INC experiments at 20 and 25°C on 50 mg of a 50:50 mixture of AN and SDIC in air

Table 2 The Limiting Friction Load of Various Mixtures of AN and SDIC

Mass ratio of AN to SDIC in mixture	Limiting load/N
20:80	>360
33:66	360
40:60	>360
50:50	360
50:50 (repeat)	240
80:20	>360

creasing the proportions of AN to SDIC from equal mass proportions was found to increase the sensitivity of the mixture to friction.

Sensitivity to Electrostatic Discharge (ESD)

The 50:50 mixture did not exhibit any positive responses to the ESD tests even at the highest setting on the apparatus (25 kV, 156 mJ). The results indicate that an electrostatic charge carried by a human body would not be sufficient to initiate explosive decomposition of the mixture. Note that these results do not preclude the possibility that the mixture would be initiated when subjected to a discharge of electricity greater than 156 mJ.

Conclusions

The DSC results clearly show that the thermal stability of mixtures of AN and SDIC is lower than that of the constituents, and that the thermal stability of the mixtures is further reduced when the reactants contain some moisture. ARC results indicate that the mixture self-heats to thermal runaway in humid air at temperatures as low as 37°C. Isothermal nanocalorimetry results show that the reaction proceeds at a measurable rate even at or below room temperature (20–25°C), and that the reaction produces about 0.4 kJ g^{-1} over the course of thirteen days at 25°C. Sensitivity tests indicate that mixtures will display energetic behaviour when subjected to sufficiently strong forces of impact or friction. These results suggest that accidental mixing of bulk quantities of these materials would pose a considerable hazard and should be avoided.

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