Thermal analysis of monomethylammonium nitrate [1]

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Abstract

Monomethylammonium nitrate (MMAN) was studied because it is used as a sensitizer in commercial water-gel explosives. Because of its extremely hygroscopic nature, MMAN crystals were placed in open pans in the DSC and temperature-cycled to eliminate water, so as to obtain accurate values for the solid–solid transition and for the melting point. The exothermic behaviour of MMAN was studied by isothermal and non-isothermal DSC in hermetic pans, by TGA, and also by accelerating rate calorimetry (ARC™). The results were compared to those for ammonium nitrate and the limited data on MMAN available in the literature. Extrapolation of DSC data on the onset temperature of the exotherm yields reasonable agreement with the large-scale ARC™ tests, providing evidence that the onset temperature can be considered as a practical parameter for hazard analysis of energetic materials.

Keywords: Thermal analysis; Monomethylammonium nitrate; DSC; ARC™

1. Introduction

Monomethylammonium nitrate (MMAN), a white, extremely hygroscopic, crystalline substance, is a sensitizer used in some commercial water-gel explosives. As such, it was of interest to us to investigate its thermal properties, and to compare it to ammonium nitrate, which is the main ingredient in most water-gel and emulsion products presently manufactured.

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Miron [1] carried out DSC, TGA and mass spectrometry on MMAN crystals. In the DSC tests, which were carried out in static air, she observed an endotherm at about 80°C, which was attributed to a solid-phase transition. A second, very broad endotherm occurred at about 110°C only when water was present; thus it was attributed to "the desorption of water with concurrent dissolution of MMAN in its desorbed water". No endotherm was observed which could be assigned to melting, which had been stated [2] to occur at 110°C. A third very broad and large endotherm started at about 150°C, which was considered to be due to the dissociation of MMAN. An exotherm started at about 250°C, which was attributed to the reaction of methylamine with oxygen.

2. Experimental

DSC tests were carried out using a TA 2100 Thermal Analyst with hermetic aluminium pans in the standard cell on either the DSC 910 or 2910 modules and nitrogen purge of 50 ml min^{-1}. Each instrument was calibrated for each heating rate using indium, lead and zinc, according to ASTM standards. A few tests were also carried using a TA Hi-Res 2950 TGA; the sample was placed on a platinum pan; N_2 was used as the purge gas at 100 ml min^{-1}. The accelerating rate calorimeter (ARC™), an automated instrument developed for thermal hazard evaluation [3] and manufactured by Columbia Scientific Industries, was used with titanium sample containers kept under constant volume conditions in an atmosphere of nitrogen. The pressure was monitored throughout the ARC™ experiments.

3. Results and discussion

3.1. DSC endotherms

The DSC curve of MMAN in a hermetic pan (Fig. 1) shows two endotherms, the first reasonably sharp and the second broad and variable, and a large exotherm. The part below 150°C is similar to that reported by Miron, but the prominent endotherm at about 240°C was not observed. The problem with MMAN, as pointed out by Miron [1], is its extreme hygroscopicity, making it impossible to expose it to the atmosphere, even momentarily, without it absorbing moisture. In order to eliminate water from the sample, it was placed in a hermetic pan without a lid in the DSC and cycled from 20 to 120°C four times. The DSC curve (Fig. 2) shows that, after the first cycle, the results were quite reproducible. The second endotherm became sharp, as would be expected for the melting point of a pure substance. Its mean extrapolated onset temperature, which should be the same as the melting point, was 108.8 ± 0.5°C, which is in good agreement with the melting point of 110 ± 2°C quoted by Parker [2]. The maximum of this peak was at 110.8 ± 0.5°C; the corresponding exotherm peak on cooling occurs about 7°C lower, as would be expected on supercooling a pure substance. The area under the peak was the same on heating and cooling yielding, $\Delta_{fus}H = 43 \pm 2$ J g^{-1}.

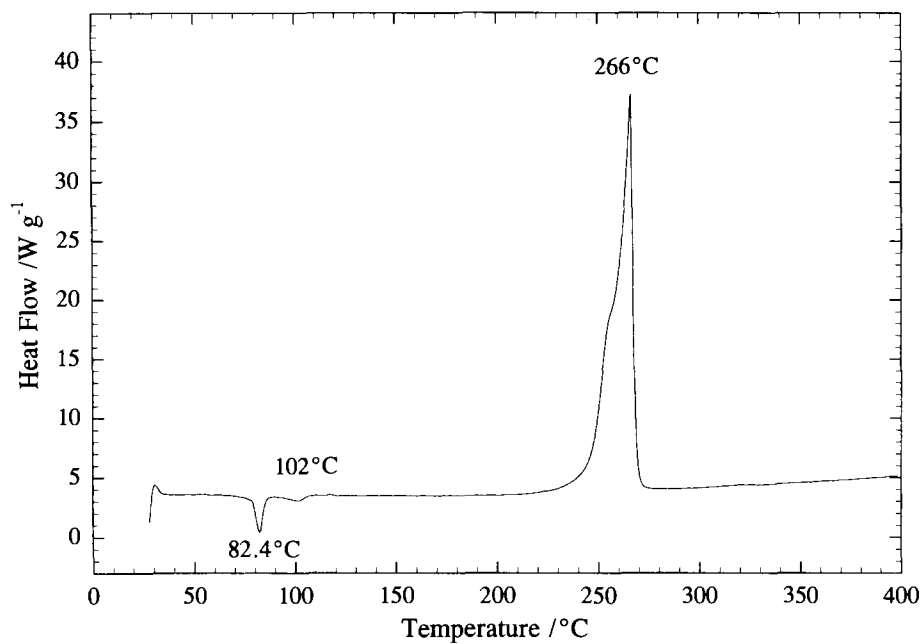Fig. 1. DSC curve of 0.462 mg of MMAN in a hermetic Al pan at a heating rate of $10°C \ min^{-1}$ and an N_2 purge of 50 ml min^{-1}.

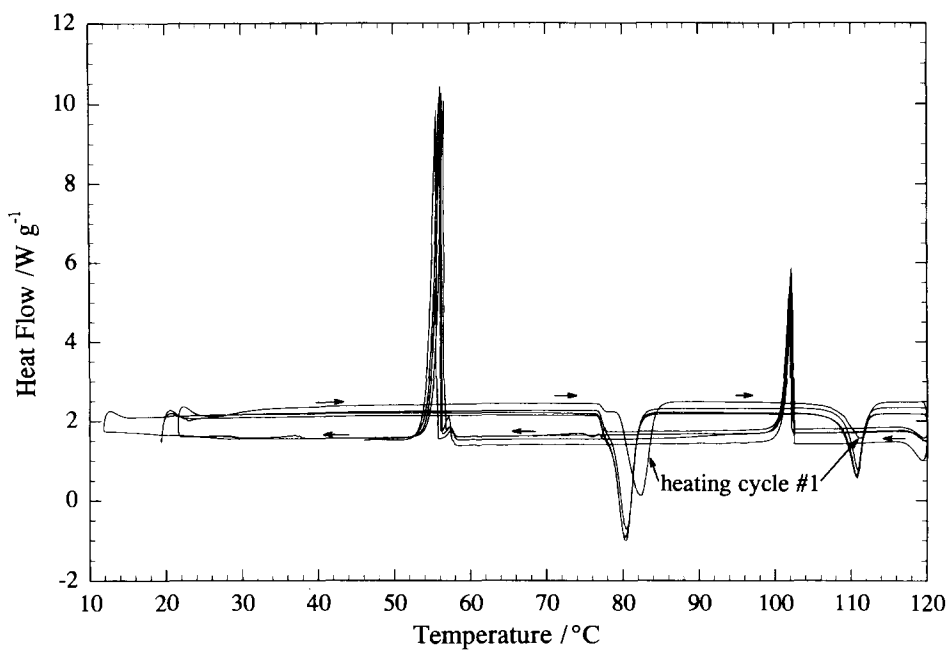Fig. 2. Heating/cooling cycling of 0.766 mg MMAN in an open Al pan at a heating rate of $5°C \ min^{-1}$ and an N_2 purge of 50 ml min^{-1}.

Hence, the existence of the melting point appears to be quite definitive; its occurrence close to the boiling point of water and the hygroscopicity of MMAN cause interference with the peak if the sample is exposed to the atmosphere. The melting point of MMAN is lower than the melting point of ammonium nitrate (AN), 109°C vs. 169.6°C [4], but its $\Delta_{fus}H$ is similar (6.8 vs. 6.1 kJ mol^{-1} [4]). The different results obtained by Miron [1] can probably be attributed to the use of non-hermetic pans operating in static atmospheric air, which would contain some moisture.

The first endotherm is due to a solid–solid transition; it also appears to be affected by the presence of water, as seen from the difference between the first and succeeding cycles shown in Fig. 2. The mean extrapolated onset temperature is 78.3 ± 0.3°C (compare Parker [2], 82°C); the maximum occurs at 80.4 ± 0.1°C; and the ΔH of the peak is 96 ± 3 J g^{-1}. The peak appears to be complex, both in cooling and heating; however, the results with respect to a possible small additional peak were not reproducible. Samples of MMAN were cooled down to -70°C; no additional transitions of MMAN were observed. (In samples that had not been heated to 120°C prior to cooling, a transition at 0°C was observed, due to water.) The phase transitions of AN are complex and remain a subject of current research [5]; it is well known that they are affected by the presence of water. For the purpose of comparison with the present work on MMAN, the phase transition I → II in AN occurs at 125°C [4], with a ΔH of 4.1 kJ mol^{-1}, compared to 80°C and 14.9 kJ mol^{-1} for MMAN.

3.2. Heat capacity

For obtaining values of the heat capacity, the DSC 2910 was calibrated using sapphire between 40 and 140°C. Using the same sample container and averaging the results after cycling as above, the values of heat capacity were (in J g^{-1} K^{-1}): 1.66 at 40°C, 1.81 at 60°C and 2.04 at 120°C. These values are similar to AN [4]: 1.67 at 0°C, 1.73 at 50°C and 1.79 at 100°C.

3.3. DSC tests: onset temperatures

The exotherm (Fig. 1) peaks at about 270°C, reasonably close to the 285°C maximum in DTA by Parker [2], and has a similar shape, i.e. with a shoulder on the low-temperature side. Miron's hypothesis [1] that this exotherm is due to the reaction of methylamine and oxygen cannot be applicable in our tests since there was no evidence of an endotherm due to dissociation; moreover, oxygen was excluded from our system. Hence, the endotherm peak represents the decomposition of MMAN, with the understanding that the mechanism is probably complex.

Although the extrapolated onset temperature has a physical meaning for endotherms, it does not have such for the exotherms: the parameter of interest, particularly for hazard analysis, is the "true" onset temperature, which is defined as the first deviation from the baseline, and is usually substantially lower than the extrapolated onset; for MMAN, the difference is roughly 20°C. Unfortunately, the value of the true onset cannot be determined as precisely as the extrapolated onset; nevertheless, "onset" in this paper refers to the true onset temperature.
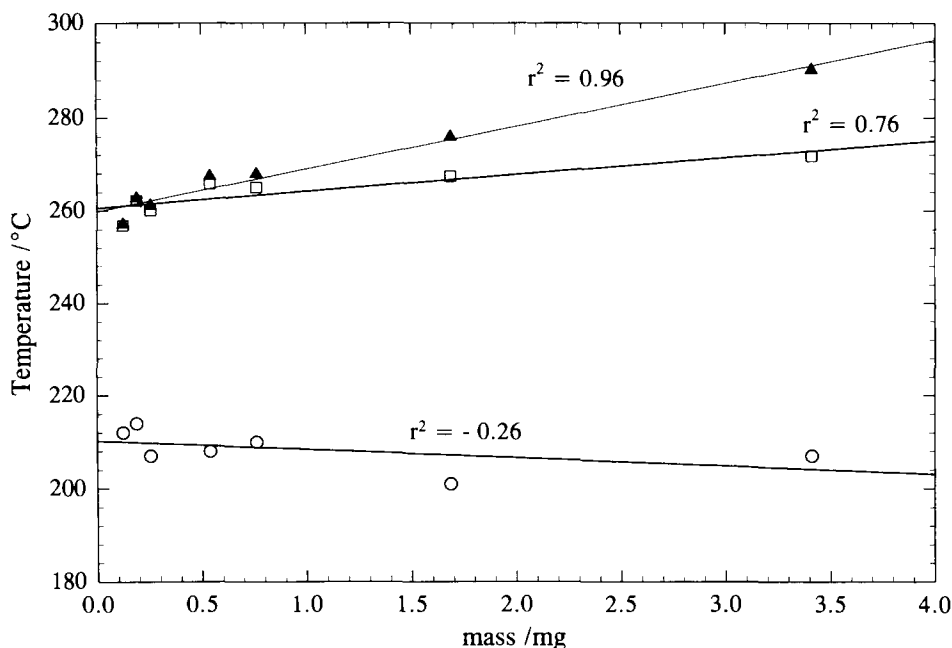
Fig. 3. The effect of sample size of MMAN on the onset temperature of its exotherm (○), the peak temperature (□) and the corrected peak temperature (▲): heating rate, $10°C$ min^{-1}; N_2 purge, 50 ml min^{-1}.

The effect of sample size on the onset and peak temperatures is shown in Fig. 3, for DSC tests carried out at $\beta = 10°C$ min^{-1}. The uncertainty in the individual onset temperatures is $\pm 5°C$, for the peak temperatures, about $\pm 2°C$. The onset temperature does not appear to be significantly dependent on sample size throughout the possible range. However, the peak temperature does appear to depend on sample size, particularly when the correction is made for the temperature lag, according to the ASTM procedure [6]. Presumably, this effect is related to the rate of thermal conduction inside the sample, because the rate of heat flow is much greater at the peak height than at its onset; thus, the extrapolated value to zero mass should be the "true" value. Based on this hypothesis, the slope of the curve, i.e. the error, would be expected to increase with increasing heat rate. Note that the effect of sample size refers only to experimental artifacts in the DSC; the intrinsic effects of sample size were measured by using the ARC with sample sizes 2–3 orders of magnitude larger.

Fig. 4 shows that both the extrapolated and true onset temperatures are mild functions of the heating rate; the true onset temperature extrapolated to zero heating rate is probably the most fundamental parameter. Unfortunately, the uncertainty in its value, from a linear least-squares fit, is rather large: $\pm 10°C$. The data suggest that a straight line is not an accurate representation at very low heating rates; the curves perhaps slope downwards. This is supported by isothermal tests, following the ASTM two-hour constant-temperature stability method [7], except allowing the trial to
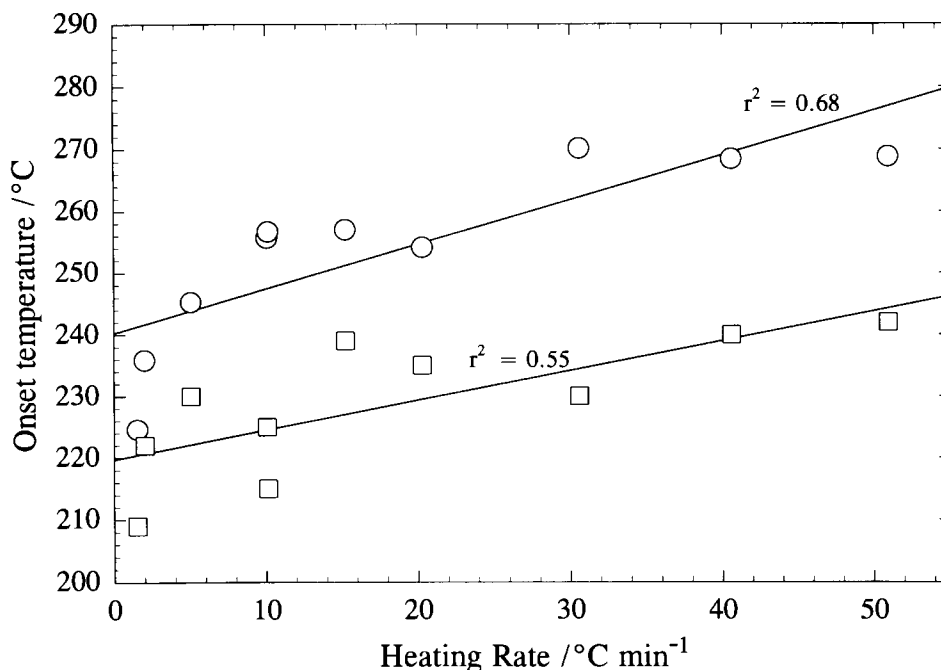
Fig. 4. Extrapolated onset temperatures (○) and true onset temperatures (□) of the exotherm of MMAN as a function of heating rate, using hermetic Al pans: N_2 purge, 50 ml min^{-1}.

continue until the beginning of the exotherm is observed. Exothermic decomposition was observed as low as 180°C, significantly lower than the onset temperature from the heating rate test. In order to extrapolate to infinite time, *i.e.* to determine the lowest temperature at which decomposition can start, the onset temperature was plotted against reciprocal time (Fig. 5) to yield 185 ± 15°C. This value is significantly lower than the values obtained from DSC curves obtained at the commonly used heating rates.

3.4. Onset temperatures by accelerating rate calorimetry (ARC™)

The principle of the ARC™ is that the bomb containing the sample is held under adiabatic conditions, by continuously adjusting the temperature of the calorimeter to the temperature of the bomb (as measured by a thermocouple attached to the outside of the bomb) so as to have zero heat flow. When the self-heating rate reaches a preset value, usually 0.02°C min^{-1}, the system enters the "exotherm" model and collects the data. A major complication with the ARC™ is that the heat generated by the sample is partly absorbed by the bomb; the ratio is given by the thermal inertia Φ

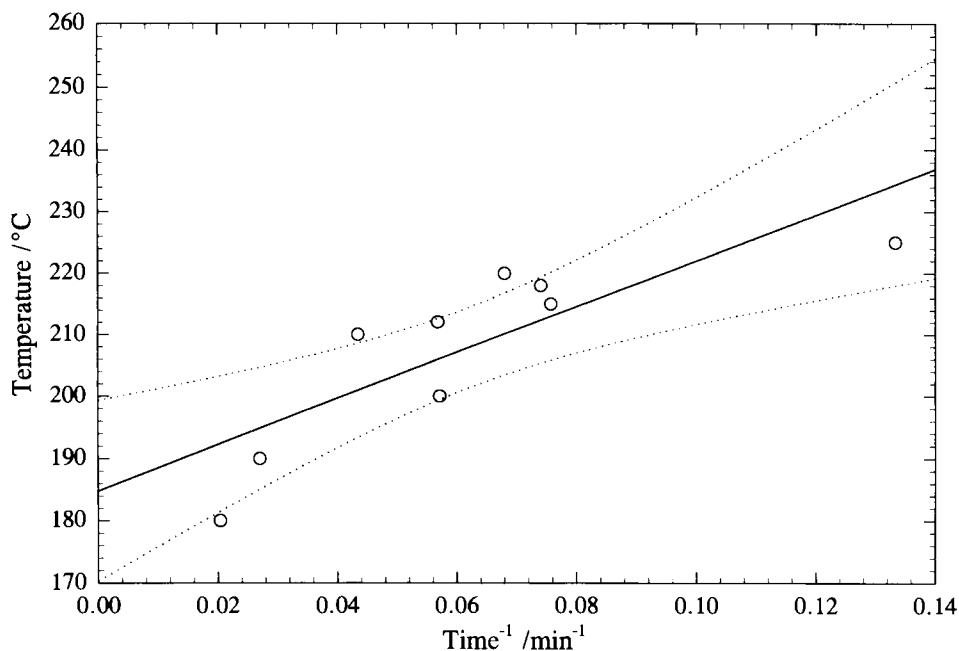$$\Phi = 1 + \frac{m_b c_b}{m_s c_s}$$

Fig. 5. Onset times of the exotherm from isothermal tests on MMAN, using Al hermetic pans in the DSC; the dotted lines are the 95% confidence limits.

where m_b is the mass of the bomb, m_s is the mass of the sample, c_b is the specific (volume) heat capacity of the bomb and c_s is the specific heat capacity of the sample. For highly energetic materials, such as MMAN, it is necessary to use small quantities, which means Φ is far from the ideal of 1. Although c_s is usually approximated as the heat capacity of the reactant, it is actually the weighted mean of the heat capacities of the reactant and products, which, of course, varies throughout the course of the test. Hence, as Φ becomes larger, the uncertainty it causes in the test results increases. Although Φ is usually used for correction of the experimental temperature rise, clearly, it affects the onset temperature as well. Near the beginning of the reaction, the adiabatic self-heat is Φ multiplied by the observed self-heat rise [3]. In order to obtain the "true" onset temperature (using the adiabatic self-heating rate $= 0.02°C$ min^{-1} as the criterion), the experimental data would have to be extrapolated. Fortunately, for MMAN, this procedure is not necessary, since the experimental onset temperature is virtually independent of Φ over a very large range (Table 1). This independence from Φ, which may be applicable to other highly energetic materials, is probably due to the high activation energy of decomposition.

Fig. 6 shows the pressure and temperature during one of these trials. The temperature was raised in 5°C steps, then held at that temperature for 30 min, then checked to determine if self-heating greater than 0.02°C occurred. After the heat step to 175°C, the decomposition began, as shown by the rapid temperature and pressure rises. Fig. 7

Table 1
The effect of thermal inertia Φ on onset temperature measurements in the ARC on MMAN

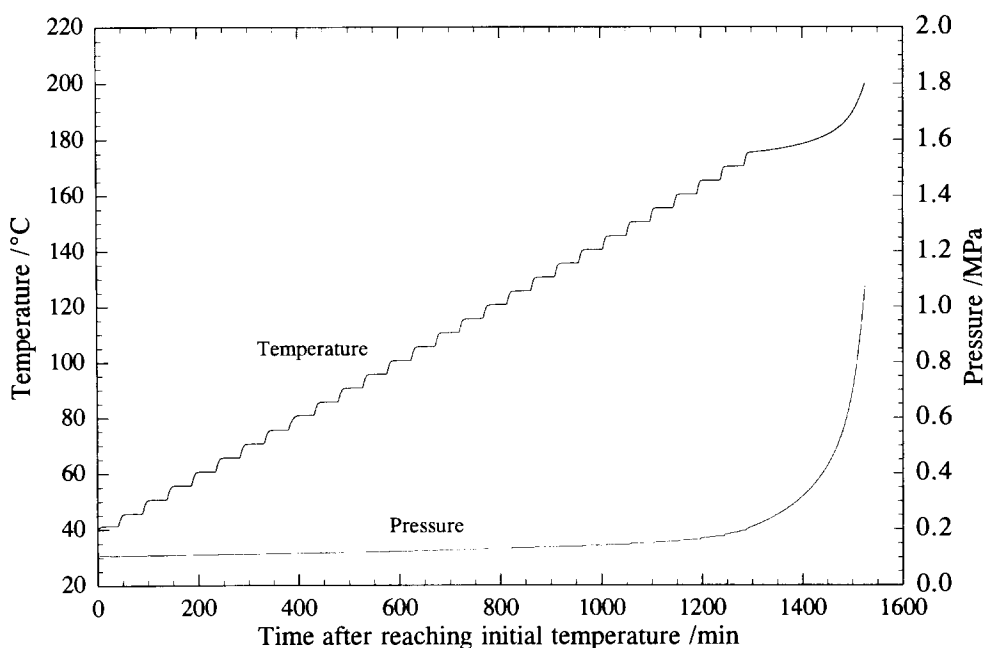| Mass /g	Φ	T_{onset} /°C	Heat step /°C
0.5856	5.7	174	5
0.4743	6.8	194	10
0.2902	10.5	175	5
0.1731	17	187	5
0.079	36	172	5
0.055	53	177	5
0.0353	82	177	5

Fig. 6. ARC™ test using 0.2902 g MMAN: 5°C heat steps; wait time, 30 min.

shows the self-heating rate on the same trial. The "spikes" are due to thermal transients which occur immediately after the heat step. It can be seen that, after the heat step to 175°C, the beginning of the exotherm, the rate increases very rapidly. If the appropriate Φ-factor of 10.5 were applied to the rate, and the data extrapolated back to the 0.02°C min^{-1}, the resultant onset temperature would be lowered only slightly, thus confirming the conclusions in the previous paragraph.

Furthermore the value obtained, 175 ± 5°C, is in good agreement with the value of 185 ± 15°C obtained from the DSC isothermal trials, which used one-thousandth of
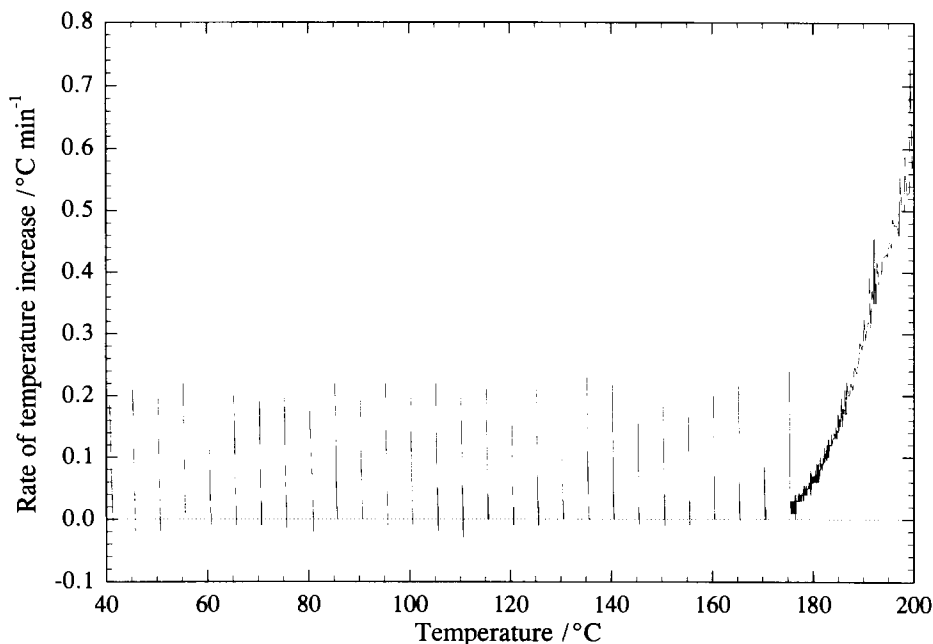
Fig. 7. Self-heating rate as a function of temperature, for the same test as in Fig. 6.

the mass. The reason for this agreement can again probably be attributed to the high activation energy of the decomposition.

3.5. Arrhenius parameters for the decomposition of MMAN from DSC

The Arrhenius parameters for the decomposition of MMAN were determined from the variation of the peak temperature with heating rate, following ASTM E698 [6]. The results obeyed the linear relationship (Fig. 8), and yielded $E = 153 \pm 6$ kJ mol^{-1} and $\ln [Z/\text{min}^{-1}] = 33.5 \pm 1.4$.

Another method of analysis used the TA isokinetics program [8]. The entire exothermic peak was generated by nine isothermal trials at temperatures between 209 and 241°C. The data were fitted by the program to both an nth-order and an autocatalytic model. The former did not yield satisfactory answers. Although the fit of the latter for each individual trial was rather poor, overall the uncertainties were reasonably small and the Arrhenius constants were fairly close to those determined by the ASTM method given in the previous paragraph: $E = 140 \pm 6$ kJ mol^{-1}, $\ln [Z/\text{min}^{-1}] = 31.3 \pm 1.5$. The orders of the reaction were: $n = 0.022 \pm 0.012$; $m = 0.24 \pm 0.06$. The validity of the values of the orders is suspect; probably the Arrhenius parameters are not very dependent upon them, but there is little documentation provided with the program to evaluate this issue. The irregular shape of the exotherm peak (see Fig. 1) also causes a problem in using this program. Note that, by
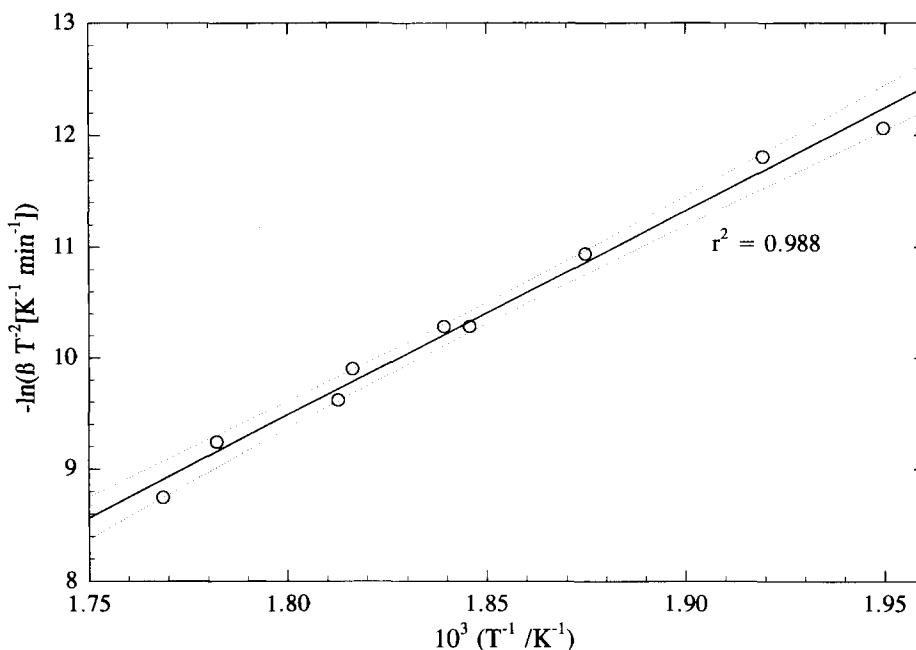
Fig. 8. Determination of Arrhenius parameters of decomposition of MMAN using ASTM E698: $E = 153 \pm 6$ kJ mol^{-1}; ln $[Z/\mathrm{min}^{-1}] = 33.5 \pm 1.4$.

necessity, these trials were carried out at lower temperatures and over a smaller temperature range than those for the ASTM method.

In order to obtain kinetic data from ARC™ trials, the reaction must go to completion while the system is maintained in an adiabatic condition. With the larger amounts of MMAN, this requirement could not be fulfilled, because the self-heating rate became too great. The standard ARC™ analysis is based on the assumption that the concentration of reactant during the test can be represented by temperature differences. However, the data, even with small quantities of MMAN, cannot be fitted to this model, probably because the reaction is complex (as can be seen by the DSC exotherm peak). Using part of the data only and restricting the analysis to the adiabatic portion, the Arrhenius parameters varied progressively from lowest to highest sample sizes: $E = 170 \to 274$ kJ mol^{-1}; ln $[Z/\mathrm{min}^{-1}] = 40 \to 68$. It is of interest that the best agreement with the DSC studies occurred for the lowest sample sizes. Further work should be carried out to explore this problem.

3.6. TGA tests

Fig. 9 shows that mass loss begins at about 115°C, no doubt due to desorption of water. (The magnitude of this loss will depend on the dryness of the sample. In a separate trial, a sample reached constant weight (3% loss) after being held for 100 min
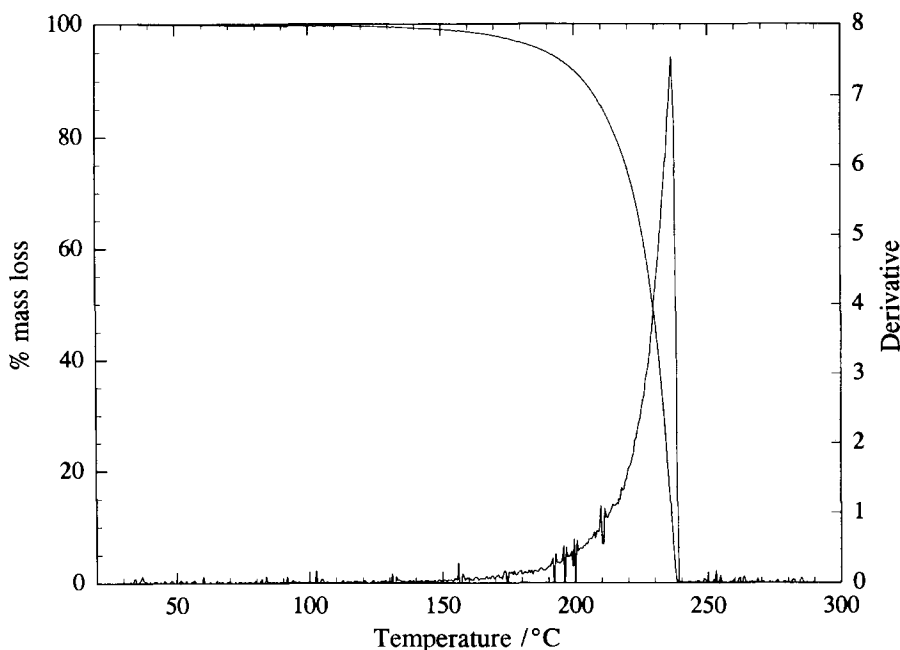
Fig. 9. TGA of 1.579 mg of MMAN.

at 120°C). This particular TGA instrument automatically decreases its heating rate as the rate of mass loss increases, thus providing data closer to the "true" transition temperature. Rapid mass loss begins at about 190°C and peaks at 236.0°C, with the sample completely gone by 238°C. This temperature of the peak rate is close to the peak maximum of 239.8°C obtained at the lowest heating rate used in the DSC, $1.5°C min^{-1}$. The peak rate obtained by Miron [1] in the TGA occurred at a somewhat higher temperature, about 280°C; this difference can probably be attributed to the differences in effective heating rates.

4. Conclusions

The concept of onset temperature, although it is not a thermodynamic quantity, has been shown by the agreement between the values obtained by DSC and ARC™ on MMAN to be a useful practical parameter for hazard analysis, because it is indepen- dent of sample size over a wide range. Although this independence was determined only for MMAN, it is probable that it will apply to other energetic materials that have high activation energies.

The problem of the discrepancy in the DSC curves of MMAN reported in the literature has been resolved; a technique of temperature cycling in the DSC with an

inert purge gas allows the elimination of effects due to absorbed water. The melting point of MMAN is $108.8 \pm 0.5°C$, $\Delta_{fus}H = 43 \pm 2$ J g^{-1} and the solid-solid phase transition occurs at $78.3 \pm 0.3°C$, with a ΔH of 96 ± 3 J g^{-1}. The onset temperature of the exotherm is $175 \pm 5°C$.

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