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INFLUENCE OF THE HEATING RATE IN THE THERMAL DECOMPOSITION OF HMX

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Abstract

This work refers to a study of the thermal decomposition of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) by differential scanning calorimetry (DSC) in non-isothermal conditions, with heating rates from 1 to 25°C $\min^{-1}$. The influence of the heating rate, the particle and the sample size were verified. The activation energy was calculated using the peak temperature shift method, proposed by Ozawa and a significant variation in the results was observed according to the range of the used heating rates. As the heating rate was increased, different conversions and self-heating effects were observed at the respective DSC peaks, indicating that the use of this method was inadequate and it may lead to incorrect results, which, in turn, could explain the wide range of activation energy values published in literature. At lower heating rates HMX decomposition occurs on the solid state and at higher ones decomposition occurs after melting practically at the same temperature, which does not depend on the heating rate.

Keywords: DSC, HMX, thermal decomposition

Introduction

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is a high explosive applied in plastic bonded explosives (PBX), propellant double base and propellant composite because of its high calorific potential, high density and smokeless combustion products [1].

Thermal decomposition of HMX has been the subject of extensive studies for many years. The complexity and dependence on the experimental conditions, physical state, temperature, pressure and its variation rates, are well known [2, 3]. The knowledge of the decomposition kinetic supplied the previous informations required to evaluate critical conditions of thermal explosion [4] and it has also been used in studies of compatibility with additives [5].

Techniques of thermal analysis such as DTA, TG and DSC have been largely used in the study of explosive decomposition kinetics in isothermal and non-isothermal conditions [4–7]. Due to the variety of techniques and methods used to calcu-

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late it, there is a wide range of activation energy values found in literature varying from 42 to 1072 kJ mol^{-1} [8].

Ozawa method [9], known as the peak temperature shift method, was developed considering that the conversion at the peak is constant and almost independent of its absolute temperature. In this way the logarithm of the heating rate is a linear function of the reciprocal value of the peak absolute temperature in first order reactions and the activation energy can be calculated from the corresponding slope. This method has been used in the study of HMX decomposition kinetics but with very different results [8, 10]. These results were obtained using a wide range of heating rates.

The purpose of this work was to verify the influence of the heating rate range on the thermal decomposition of HMX. The effect of particle size was also investigated and thermogravimetry (TG) was used as well in order to help the interpretation of DSC curves. Ozawa method was used as part of a preliminary study for selecting the best method for calculating the kinetic parameters.

Experimental

This work was performed with a Perkin Elmer DSC7 at the heating rates of 1, 2, 3, 5, 7, 10, 15, 17, 20, 22 and 25°C min^{-1} from 80°C up to the end of the decomposition. DSC measurements were conducted by placing 2.5 mg of pure HMX in an aluminum pan with perforated cover under nitrogen atmosphere (40 ml min^{-1}). TG measurements were performed with a TGA-951 DuPont with 5.5 mg placed in a platinum pan, using heating rates of 2 and 25°C min^{-1}. Three runs with each sample were made for each heating rate.

The investigations of the decomposition kinetics were done with three different samples. One sample with bimodal particle size distribution, M2, (60% with average diameter of 173 μm and 34% with average diameter below 40 μm); and two samples with unimodal particle size distribution, R65 (average diameter of 210 μm) and R200 (average diameter below 75 μm).

Results

Figures 1 and 2 show DSC curves of sample M2 decomposition at several heating rates. The curves were presented in the range 250–300°C for better visualization, but endothermic peaks in the range 185–200°C due to β-HMX → δ-HMX phase transition [1] were observed. HMX decomposition is exothermic. As the heating rate was increased, the peaks were shifted to higher temperatures changing their shape.

Figure 1 shows that at lower heating rates (1 to 5°C min^{-1}) the decomposition of HMX begins in a mild way and there is a shoulder before the peak. At 7°C min^{-1} there is a change in the shape of the curve, the shoulder before the peak disappeared completely, and at 10°C min^{-1} a weak exothermic decomposition followed by an endothermic peak due to HMX melting is verified before the strong exothermic decomposition.

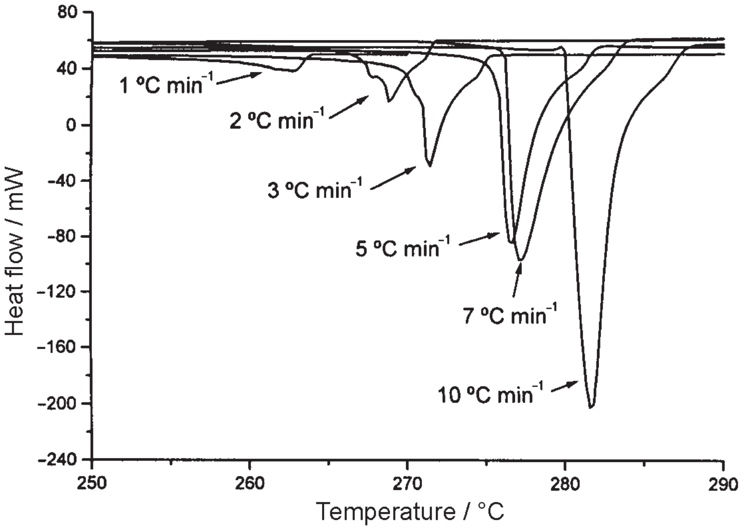

Fig. 1 DSC curves of sample M2 decomposition (1 to 10°C min^{-1})

Figure 2 shows higher heating rate (15 to 25°C min^{-1}) results, where it is observed that the endothermic peak becomes more defined and the exothermic part before it, which occurred at 10°C min^{-1}, is not observed any more. The decomposition occurred strongly after the endothermic peak. As the heating rate was increased the HMX decomposition occurred randomly showing two exothermic peaks, not shown here, which moved away from each other as the heating rate increased.

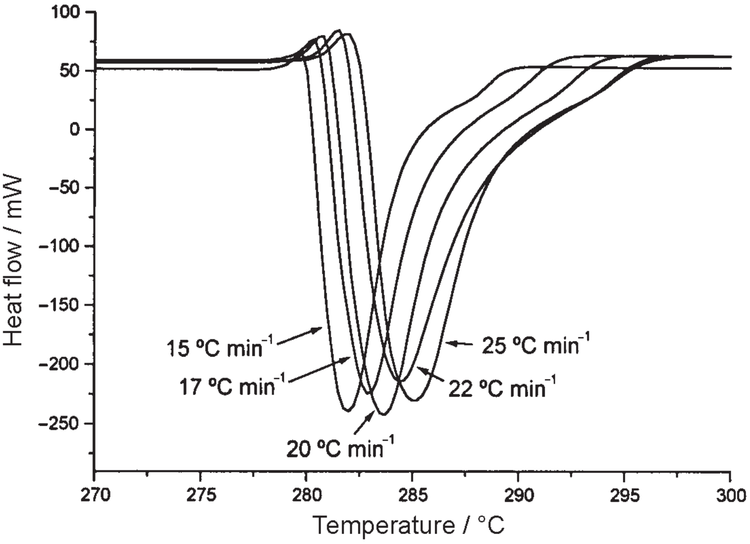

Fig. 2 DSC curves of sample M2 decomposition (15 to 25°C min^{-1})

The behavior of the samples with unimodal particle size was similar and the decomposition temperatures of the larger particles (R65) were lower than those of smaller ones (R200).

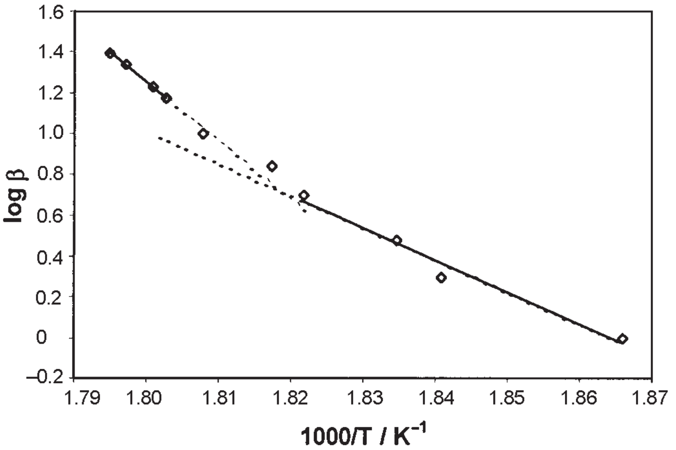

Fig. 3 Ozawa's plot with temperature of single peak of M2

The activation energy was calculated by Ozawa's plot [9], shown in Fig. 3, where β is the programmed heating rate and T is the absolute temperature of the peak. This plot was done using the data from single peak DSC curves of sample M2. The value of the activation energy (E) is calculated by the equation E=2.19R[dlogβ/d(1/T), where E is the activation energy (J mol^{-1}); R is the gas constant and dlogβ/d(1/T) is the slope.

To verify the influence of the heating rate in the activation energy results, two ranges of heating rates were used because of the changes observed in DSC curve shapes (Figs 1 and 2). Heating rates of 1, 2, 3 and 5°C min^{-1} were chosen for the first range, because similar shapes observed for these rates indicated the same reaction mechanism. The behavior of the samples R65 and R200 was similar. The second range included 15, 17, 22 and 25°C min^{-1} heating rates, because at these rates their similarity was that the decomposition always occurred after HMX melting. The rates 7 and 10°C min^{-1} were not included because they were considered a transition region, as can be observed in Fig. 3.

The activation energies calculated from the slope of Ozawa's plot straightlines (Fig. 3) for the first and second ranges were respectively, 287 and 527 kJ mol^{-1} for M2; 279 and 462 kJ mol^{-1} for R200; 294 and 394 kJ mol^{-1} for R65.

Figure 4 shows TG curves at heating rates at 2 and 25°C min^{-1}, which were done in order to help the interpretation of DSC curves. It was observed that at 2°C min^{-1}, as in DSC curves, the decomposition begins in a mild way before the strong decomposition, while at 25°C min^{-1} only the latter appears with total loss mass occurring in a very short time.

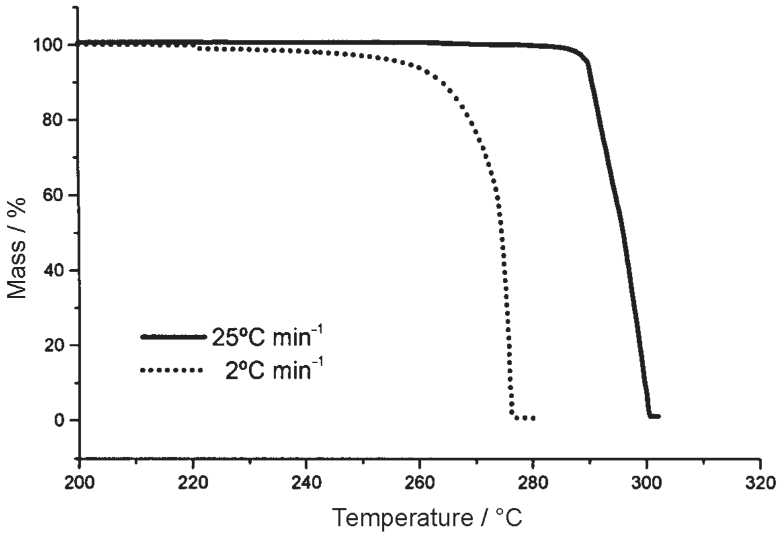

Fig. 4 TG curves of sample M2 decomposition (2 and 25°C min^{-1})

Discussion

The variation of DSC curve shape caused by heating rate change suggests that different decomposition mechanisms may occur. At low heating rates (1 to 5°C min^{-1}) the decomposition occurred at temperatures below the HMX melting (280°C). The minimum temperature of liquefaction depends on the particle and sample size and on the probability of gaseous reaction products to escape. In studies accomplished by Kraeutle [11] it was verified that the liquefaction temperature of HMX can be lower than 280°C and it is inversely proportional to particle size at constant sample size. Kraeutle verified through experiments with 2.2 mg of particles larger than 350 μm that there was no liquefaction at 266°C, which only occurred with 7.8 mg of the same sample. As the sample mass used in this study was 2.5 mg and particle size was smaller than 350 μm, it is reasonable to suppose that the decomposition until the heating rate 5°C min^{-1} occurred in the solid phase. In complementary runs we made in open pans to have visual observation, it was observed that HMX decomposition at 270°C, occurred in the solid state.

The presence of the shoulder before the peak, observed at low heating rates could be associated to two acceleratory periods. In studies of thermal decomposition of solid HMX using STMBMS (simultaneous thermogravimetric modulated beam mass spectrometer) Minier [12] verified that the main gaseous products of HMX decomposition are H_2O, N_2O, CH_2O, NO and CO and temporal behavior gas formation rates are characterized by the following sequence: 1) an induction period; 2) an increasing rate of formation between 0 and 10% decomposition; 3) a faster rate of decomposition between 10 and 30% decomposition and a decreasing rate of gas formation after 40% decomposition. A possible association of this temporal gas behavior could be done with DSC curve shape in low heating rate.

It was observed that the decomposition in the solid phase is less affected by particle size variation as shown by activation energy values obtained in this study, which agreed with values obtained by Hondee and Gosgarian referred by Kimura [8].

The transition region, around 10°C min^{-1}, observed by the change in the DSC curve shape, is confirmed by changing the straightline slope (Fig. 3). Kraeutle observed the same behavior in the decomposition of HMX under nitrogen atmosphere [10]. The inclusion of 10°C min^{-1} data to calculate the activation energy in the high heating rate set would not affect the result significantly, but because it belongs to a transition region we preferred not to include it in the calculation.

When using heating rates from 15 to 25°C min^{-1} the decomposition always occurred after HMX melting. The activation energies for high heating rates were higher than for low heating rates. Kimura obtained the same conclusion in his studies with several heating rates [8]. The value of the activation energy found in this study for high heating rates was close to Takaira and Okazaki's values, referred by Kimura [8], using non-isothermal DSC in the range of 280–300°C.

The decomposition temperature of the sample with unimodal particle size R65 was anticipated by approximately 1°C and its activation energy was lightly lower than that of R200.

It was observed that the activation energy values vary too much depending on the heating rate chosen to obtain the straightline in Ozawa's plot. In order to verify the effect of self-heating, additional runs were done with different sample sizes (0.1, 0.2, 0.5 and 1 mg) at some heating rates and important observations were done. At heating rates where HMX decomposition occurs after melting no variation was observed at peak temperature using those masses. With 0.1 mg and 25°C min^{-1} the heat flow was 4 mW and the peak temperature was the same obtained with 2.5 mg, showing that in this condition apparently there is no influence of mass. On the other hand, above 15°C min^{-1}, the beginning of melting, indicated by first displacement of baseline always occurred at about 277°C, not depending on the heating rate. Visual observations showed that, after melting, HMX decomposition is extremely fast, as it was also observed by TG analysis. It suggests that the DSC peak displacement in high heating rates could be caused only by the response time of the equipment not reflecting the real behavior of the sample.

In low heating rates it was observed that the peak temperature decreases as the sample size increases. It could be justified by the self-heating effect in larger samples which causes a run-away-reaction. Another observed factor was that the conversion at the peak, calculated by the ratio between total enthalpy and enthalpy to the peak, changes according to the heating rate. The conversion at the peak is 90% at 1°C min^{-1}; 50% at 3°C min^{-1} and 30% at heating rate above 5°C min^{-1}. These observations suggest that Ozawa method is not adequated for the evaluation of the activation energy of HMX decomposition.

About the two exothermic peaks that occur randomly at heating rates higher than 15°C min^{-1} association was not possible. The association with pan jumping due to an explosion caused by pseudoconfinement was discarded when the same behavior was observed with an open pan. However, it was verified that there is a relationship with the sample amount. DSC runs with samples of 1 mg did not present subdivision of exothermic peak. Two hypothesis were proposed: the occurrence of simultaneous endothermic and exothermic processes due to the melting and the decomposition of HMX, or the occurrence of different mechanisms from decomposition reaction.

The first hypothesis was considered unlikely because no variation in temperature onset and enthalpy of fusion was observed between two situations.

Visual observations of samples with 1 and 2.5 mg in an open pan and in a pan with perforated cover allowed to observe different decomposition mechanisms. With 1 mg sample, in both kinds of pan, there was no evolution of nitrous gas characterized by its brownish color. In the case of the 2.5 mg sample, in both conditions brown gases were observed. The brown gas was not observed only when 2.5 mg was placed in a larger pan where the grains were more separated. This suggests that aleatory occurrence of two exothermic peaks could be related to the occurrence of different mechanisms and is correlated with contact among the grains. Effects of amount and arrangement of sample over the decomposition of HMX were also observed by Kraeutle [11].

Brill, referred by Kim [13], verified that the overall decomposition mechanism of HMX could be described by the following two competitive reactions:

$$\mathrm{HMX} \rightarrow 4[\mathrm{N_2O{+}CH_2O}] \qquad \text{(R1)}$$

$$\mathrm{HMX} \rightarrow 4[\mathrm{HONO{+}HCN}] \text{ or } 4[\mathrm{N_2O{+}HCN{+}H}] \qquad \text{(R2)}$$

Reaction R1 is exothermic (-209 kJ mol^{-1}) and reaction R2 is endothermic (159 kJ mol^{-1}). During the final stage of the decomposition process, the relative concentrations of N_2O and CH_2O appeared in about the same amount as NO_2 and HCN, providing strong support for the validity of reactions R1 and R2 [13]. Behrens [14] verified an increasing of HCN evolution in the decomposition of liquefied HMX. Based in their studies the two exothermic peaks in high heating rates could be associated to competition between R1 and R2 reactions. The results observed by TG in the high heating rate cannot confirm or discard the hypothesis of association with the gas behavior and studies using GC/MS have been in progress.

Conclusions

It was observed that the heating rate is an important factor in the thermal decomposition of HMX. Above 10°C min^{-1} the decomposition occurs after melting and the heating rate doesn't have an influence on the peak temperature. At lower heating rates in which the decomposition occurs on the solid state, the effect of self-heating, according to the used sample size, was observed by the displacement of the peak temperature and mainly by the fact that the conversion at the peak is not constant. These observations indicate that the peak temperature shift method, proposed by Ozawa, is inadequate to calculate the HMX kinetic parameters.

Changes in the shape of DSC curves may indicate different mechanisms. However, the use of the above mentioned method to evaluate the activation energy may lead to wrong results depending on the used operating conditions.

The variation of the HMX activation energy values according to the considered sample mass and heating rate range, and the corresponding change and complexity of the decomposition process could be an explanation for the wide range of values observed in literature, since Ozawa method is often applied for this purpose.

The influence of the particle size was observed by the decrease of the decomposition temperature for the larger ones.

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