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THERMAL CHARACTERIZATION OF MIXTURES OF NITROTRIAZOLONE WITH HMX AND RDX[1]

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ABSTRACT

Thermal characterization of mixtures of nitrotriazolone (NTO) with octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) has been carried out by means of differential scanning calorimetry and thermogravimetric analysis. It has been found that HMX decomposition temperature remains constant through the whole composition range. However NTO decomposition temperature decreases as the NTO/HMX ratio decreases. The RDX decomposition temperature keeps constant in all compositions studied. The RDX melting temperature decreases few degrees. The NTO decomposition appears at lower temperatures as the RDX content increases.

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INTRODUCTION

As a part of a general study about explosive mixtures that we have undertaken[4,5], we have considered of especial interest the thermal analysis of the NTO/HMX and NTO/RDX mixtures. These types of mixtures, consisting of a traditional high explosive and a novel less sensitive explosive, are being considered in order to get insensitive munitions. Due to the low sensitivity of nitrotriazolone (NTO), this explosive is being proposed as a component in formulations with hexogen (RDX) and octogen (HMX) in order to get an improvement in the insensitivity of the munition[6,7].

In the development of this type of explosives it is necessary to take into account that the mixing of explosives with inert binders, as well as with other explosives, might lead to variations in the decomposition temperatures. If these temperatures get close to the process temperature, the processing of the mixture could become unsafe. Owing to this fact, a thermal analysis of the explosive mixtures must be carried out before undertaking the processing.

The instrumental techniques chosen for this study were Differential Scaning Calorimetry (DSC) and Differential Thermal Analysis (DTA) because of the simplicity of sample preparation and the good reproducibility of

results. Thermogravimetric Analysis (TG) has also been used as a complementary thermal technique. These techniques are widely used in thermal characterization of exploxives[8,9].

EXPERIMENTAL

RDX is a commercial product of Unión Española de Explosivos. HMX was synthesized in our laboratory according to Bachmann process[10]. NTO was synthesized according to method described in ref. 11. Explosive samples were purified by recrystrallization. The explosives were physically mixed and milled in order to achieve homogeneous samples. All the mixtures are reported as weight percent.

DSC and DTA analysis were carried out under helium flow using a Perkin-Elmer DSC 7 and a Mettler TA 2000, respectively, after previous calibration with indium and zinc. The heating rate applied was 10°C/min. Samples of 1 mg were placed into an aluminium pan and covered with an aluminiun disk using a crimping press. An empty aluminium pan with cover was placed in the reference sample holder. Peak temperatures were chosen due to the impossibility to determine precisely the onset temperatures. TG analysis were carried out in a Perkin-Elmer thermogravimetric analizer TGA 7 under nitrogen atmos-

phere. Samples of 1-2 mg were heated at 10°C/min from 50°C to 400°C and weight loss curves versus temperature were plotted. Temperature axes of TGA curves were calibrated using Curie point standards (alumel and nickel) and horseshoe magnet.

RESULTS AND DISCUSSION

NTO/HMX system

Thermal behavior of NTO/HMX mixtures has been studied for the whole composition range. DSC curves can be observed in Figures 1 and 2.

Thermogram of pure NTO can be observed in Figure 1 (curve a), with a decomposition temperature range between 263°C and 306°C with a maximun at 280°C. Curve b corresponds to the thermogram of NTO with 3% of HMX. A clear broadening of the decomposition range together with a peak shifting to 270°C are observed. Curve c represents the thermogram of NTO with 10% of HMX. The decomposition peak shifts to 264°C. On curve d (NTO with 40% of HMX) the HMX decomposition is already detected as a single peak at 290°C.

On the other hand, HMX decomposition is not influenced by the NTO presence and it appears at the same temperature for all compositions studied. This fact can be observed in Figure 2. Curve a is the thermogram of pure

HMX with a decomposition range between 274°C and 310°C with a maximum at 290°C. The NTO addition to HMX does not produce any effect in temperature decomposition as it can be observed in the different curves of Figure 2. Curve b is the thermogram of HMX with 10% of NTO. The HMX decomposition temperature keeps constant and the NTO decomposition is seen at 258°C aproximately. In curves c and d the increase of NTO content is clearly observed with a decomposition maximun at 255°C.

Although HMX decomposition does not depend on NTO content in the explosive mixture, the polymorphic transformation of HMX shifts to lower temperatures in the mixtures. Thus, differential thermal analysis of the mixture NTO/HMX (10/90) shows a decrease of ca. 10°C with respect to pure HMX.

Thermogravimetric analysis of the NTO/HMX system are plotted in Figure 3 and 4. According to DSC results, these curves show a decrease of the NTO decomposition temperature as the HMX content increases. The curve a of Figure 3 corresponds to weight loss versus temperature for pure NTO. The weight loss starts at 195°C and ends at 276°C with a residue of 17 % of the initial weight. The onset of this curve appears at 272°C. The next composition tested contains 5 % of HMX (curve b). The shapes of the curves are very similar, but the temperature corres-

ponding to a weight loss of 50% decreases 17°C. The trend is the same for the next composition (with 10% of HMX). For HMX content higher than 30% two different steps corresponding to both decompositions can be observed.

The TGA curves of NTO/HMX mixtures with higher content of HMX can be seen in Figure 4. Curve a corresponds to pure HMX with an onset at about 283°C. With 10, 30 and 50% of NTO content, two different steps are observed but the weight loss range of HMX keeps almost invariable.

NTO/RDX system

The same analysis was carried out for NTO/RDX mixtures and the results are somehow similar, but with a more important effect on the shifting of the NTO decomposition peak. As it can be seen in Figure 5 a clear displacement in the NTO decomposition range occurs as a result of the RDX addition.

DSC thermograms of NTO/RDX mixtures are shown in Figures 5 and 6. Like NTO/HMX system, NTO decomposition temperature decreases as the RDX content increases (Figure 5), showing a higher depression of the decomposition temperature than that of the NTO/HMX mixtures. The shifting of the NTO decomposition peak can be observed in Figure 5. For a composition of 30 % of RDX,

240°C. The existence of this sole peak is due to the fact that as the decomposition temperature of NTO decreases it overlaps the RDX decomposition (curve d). This fact is confirmed by the curve c, in which the RDX decomposition can be noticed at 242°C.

Thermograms corresponding to the NTO/RDX mixtures with a ratio NTO/RDX ≤ 1 are plotted in Figure 6. Curve a corresponds to pure RDX thermogram where melting and decomposition peaks are observed at 206°C and 242°C, respectively. With 10% of NTO an interesting fact occurs. The decomposition of NTO takes place inmediately after the melting of RDX and afterwards the RDX decomposition. With 30% of NTO content, the same effect happens. The assignment of the different decomposition peaks has been based upon their relative intesities and TG analysis. For compositions between 50% and 70% of NTO content only a broad exothermic peak is observed just after the melting process.

This behavior is not observed for the RDX decomposition, which appears always at the same temperature (242°C) as it can be seen in Figure 6. For low NTO content, decomposition takes place between the melting and the decomposition of RDX (Curves b and c Figure 6).

In Figures 7 and 8, thermogravimetric analysis of

NTO/RDX mixtures are plotted. For NTO/RDX mixtures with 10% of RDX, two steps are observed, corresponding to RDX and NTO decomposition. With 20% of RDX two steps can still be notice. But for higher content of RDX only one step can be seen. In figure 8, two steps can also be observed for explosive mixtures with low content of NTO. The first step corresponds to NTO decomposition. This fact is in agreement with that observed in the DSC plot of these mixtures, which shows that NTO decomposition takes place between the melting of RDX and its decomposition. As it happened in the case of HMX, the weight loss due to RDX decomposition takes place in the same temperature range, independently of the mixture composition.

The variation in the pattern of the TG plots as a function of the composition of the explosive mixture can be explained taking into account that although decomposition temperatures of pure NTO and RDX are very different, as NTO decomposition shifts to lower temperatures, it goes through the RDX decomposition temperature range.

CONCLUSIONS

Composition dependences of decomposition temperatures for NTO/HMX mixtures are plotted in Figure 9. HMX

decomposition temperature remains constant through the whole composition range. However NTO decomposition temperature decreases as the NTO/HMX ratio decreases. The temperature decrease can reach 25°C. This dependence is not linear and is specially remarkable for low contents of HMX.

Decomposition and melting temperatures as a function of composition for NTO/RDX mixtures are plotted in Figure 10. RDX decomposition temperature keeps constant in the whole composition range. RDX melting temperature decreases from 206°C up to 201°C for a NTO content of 30% and keeps constant for higher contents. As it has been mentioned above, the NTO decomposition appears at lower temperatures as the RDX content increases. At compositions between 50% and 70% of NTO, only one broad exothermic peak is observed.

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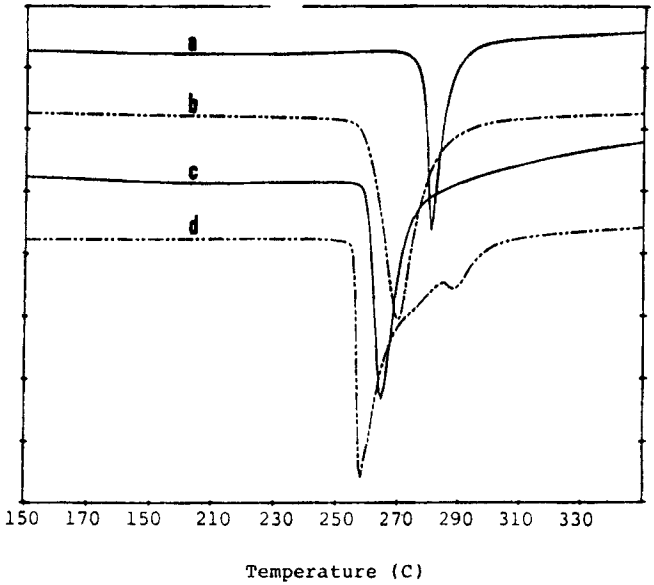

Figure 1

DSC curves of NTO/HMX mixtures (a: 100/0, b: 97/3, c: 90/10, d: 60/40).

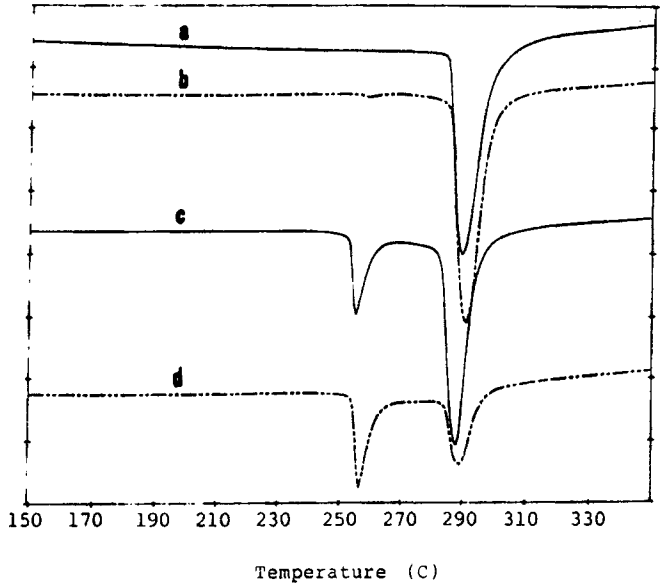

Figure 2

DSC curves of NTO/HMX mixtures (a: 0/100, b: 10/90, c: 30/70, d: 50/50).

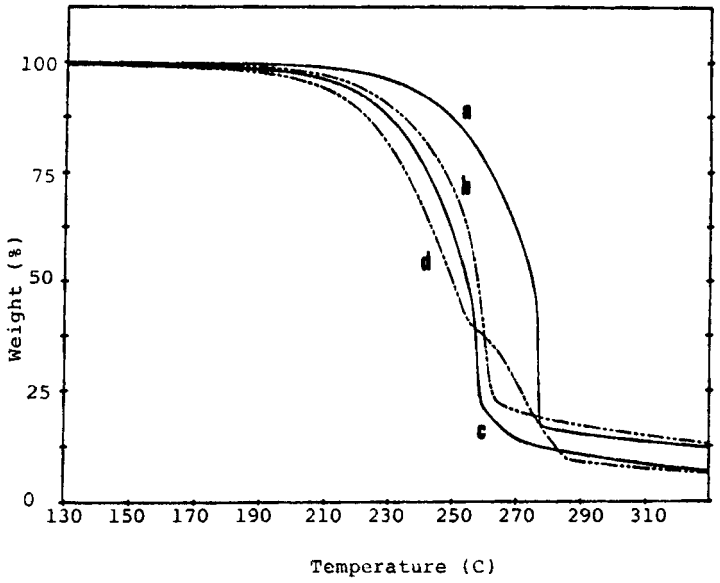

Figure 3

TGA curves of NTO/HMX mixtures (a: 100/0, b: 95/5, c: 90/10, d: 70/30).

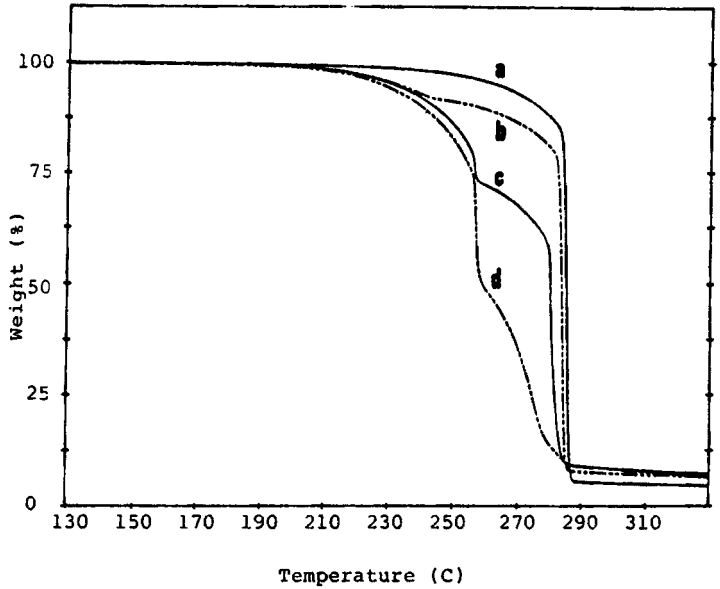

Figure 4

TGA curves of NTO/HMX mixtures (a: 0/100, b: 10/90, c: 30/70, d: 50/50).

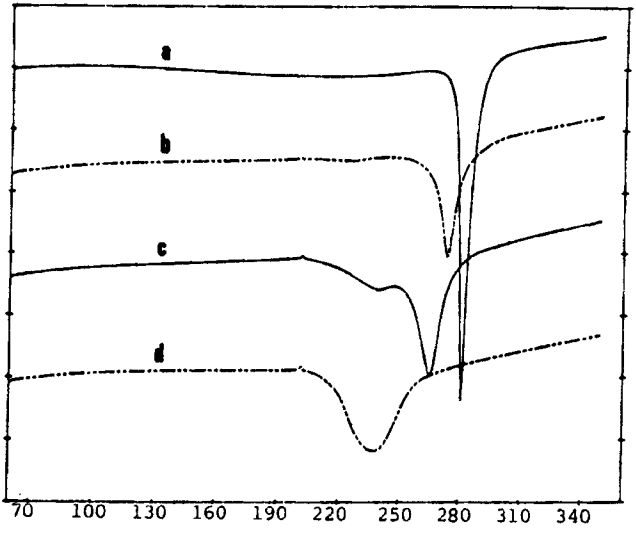

Figure 5

DSC curves of NTO/RDX mixtures (a: 100/0, b: 90/10, c: 80/20, d: 70/30).

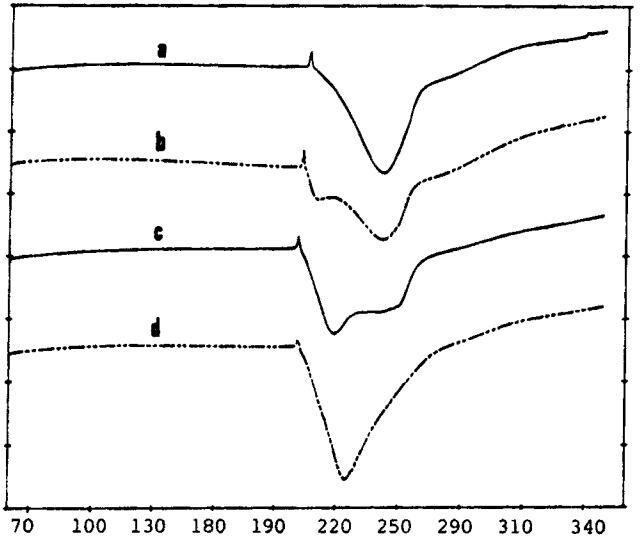

Figure 6

DSC curves of NTO/RDX mixtures (a: 0/100, b: 10/90, c: 30/70, d: 50/50).

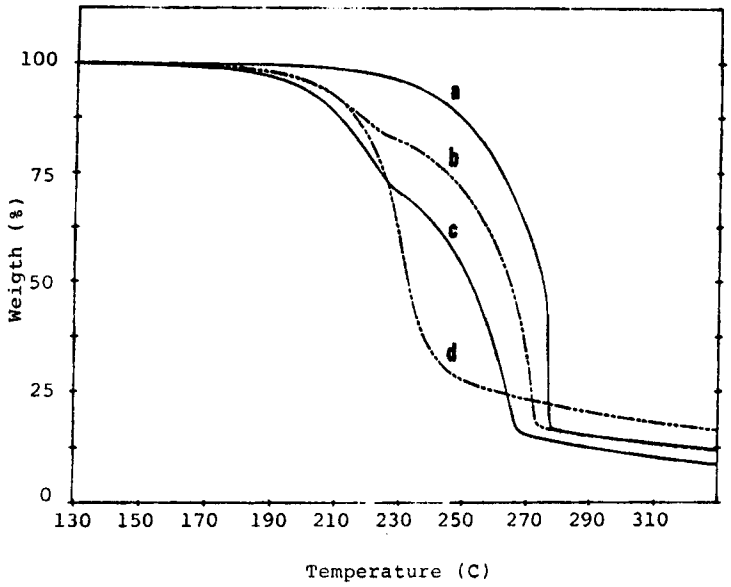

Figure 7

TGA curves of NTO/RDX mixtures (a: 100/0, b: 90/10, c: 80/20, d: 70/30).

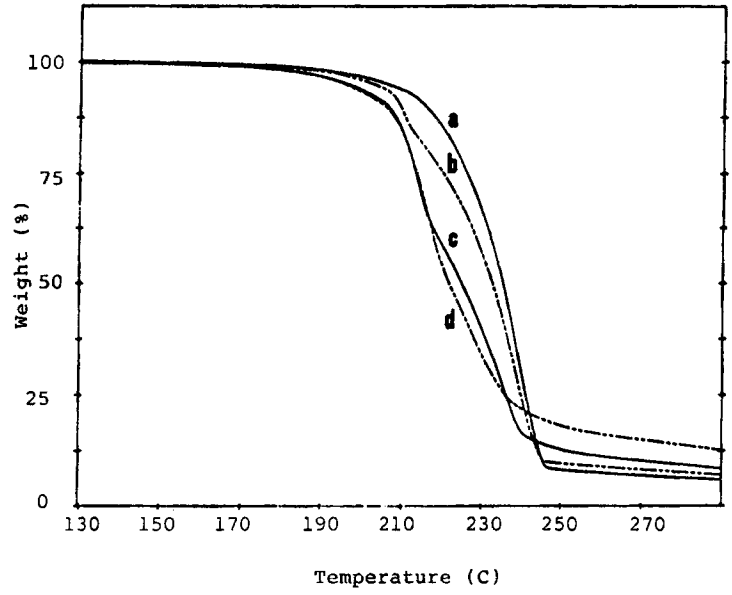

Figure 8

TGA curves of NTO/RDX mixtures (a: 0/100, b: 10/90, c: 30/70, d: 50/50).

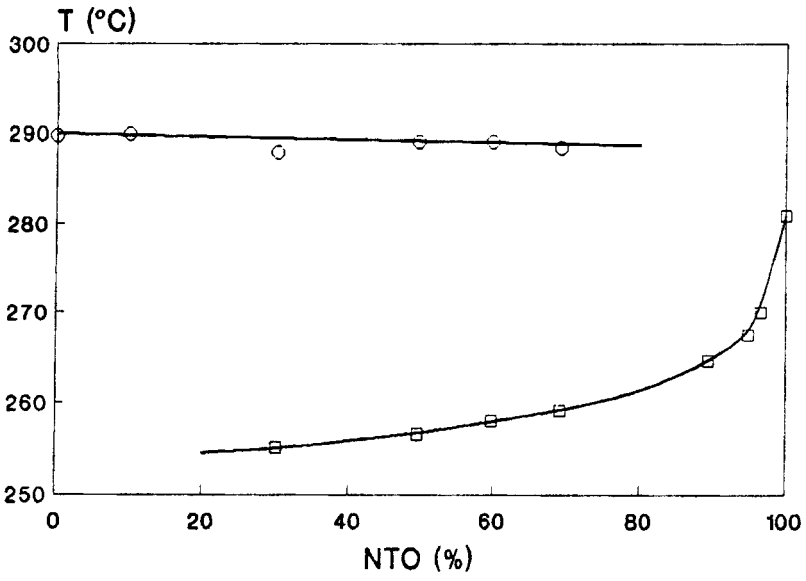

Figure 9

Decomposition temperatures of NTO (□) and HMX (o) as a function of the NTO content for NTO/HMX mixtures.

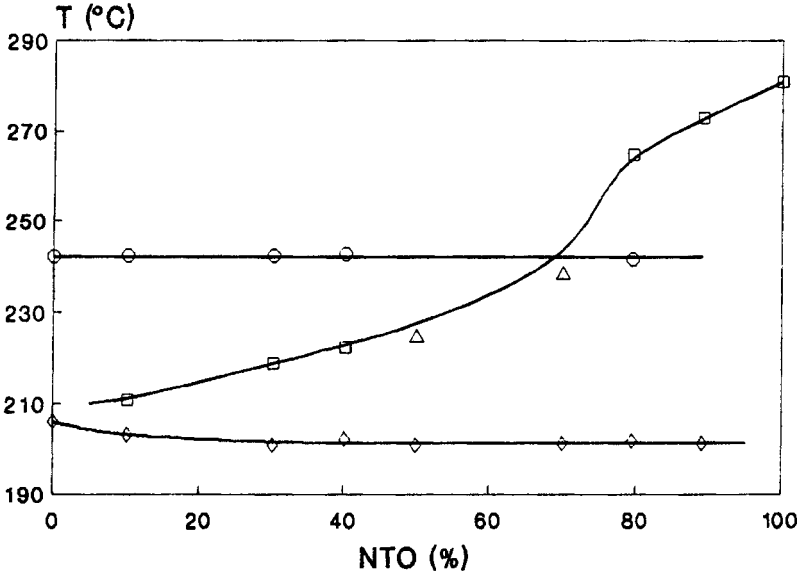

Figure 10

Decomposition temperatures of NTO (□) and RDX (o), and RDX melting temperatures (◊) as a function of the NTO content for NTO/RDX mixtures. At 50% and 70% of NTO a sole decomposition peak is observed (Δ).