

Sensitization of PETN by Oxalic acid – A DSC study

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Abstract

Pentaerythritol tetranitrate (PETN) is a commonly used secondary high explosive in various industrial and military munitions. The stability and chemical compatibility plays a vital role in use of this explosive material. Earlier studies show the presence of other compounds effect the thermal stability of high energetic materials. The present work is aimed at studying the changes in decomposition pattern of PETN in presence of Oxalic acid (OA). Results provide clue about the manner in which the decomposition takes place and the nature of intermediate products that are being formed during the course of decomposition.

Keywords: Chemical compatibility, Thermal decomposition, Pentaerythritol tetranitrate (PETN), Oxalic acid

1. Introduction

The study of thermal behavior of high energetic materials is of great interest as it indicates the sensitivity, shelf life and thermal stability of the materials. Presence of some additives greatly influences the thermal stability of high energetic materials. The effect of additives on RDX¹⁾, and HMX²⁾, effect of amines on nitro compounds^{3), 4)}, and decomposition mechanism of nitro, nitramine and nitrate explosives have been reported in literature⁵⁾. A lot of work has already been carried out on the decomposition of PETN and the effect of various additives on its decomposition, using various thermal and spectroscopic techniques⁶⁾. The action of weak base on TNT has been investigated by E.E. Kilmer⁷⁾. In the present study the sensitization of Pentaerythritol tetranitrate (PETN), which is a commonly used secondary high explosive, by organic weak acid (oxalic acid) has been investigated using Differential Scanning Calorimetric (DSC) technique.

2. Methods and materials

2.1 Materials

Pentaerythritol tetranitrate - Procured from M/s IDL Industries, Hyderabad, India.

Oxalic acid - Oxalic acid dihydrate, (COOH)₂. 2H₂O, Analyzed Reagent, Ranbaxy, minimum assay 99.8 %.

2.2 Operating conditions

Differential scanning thermograms were recorded at a heating rate of 20°C min⁻¹ using a PerkinElmer Pyris 1 DSC with Nitrogen (IOLAR-2) as purge gas flowing at the rate of 20 ml min⁻¹. The temperature calibration of the instrument was referenced to the melting points of two standard samples. Viz. Indium (156.6°C), and Zinc (419.47°C).

2.3 Sample preparation

The samples of required composition were prepared by grinding the components with mortar and pestle (Table 1). All the samples were accurately weighed using PerkinElmer AD-6 auto balance and sealed in aluminum pans using a crimping device.

3. Results and discussions

The exothermic and endothermic peak temperatures of all the seven mixtures obtained from the recorded thermograms are listed in Table 2.

Table 1 Sample and their mixtures in different ratios.

Composition	Ratio (w/w)
PETN	Neat
OA	Neat
PETN and OA	5:1
PETN and OA	5:2
PETN and OA	5:3
PETN and OA	5:4
PETN and OA	1:1

Table 2 Exothermic and endothermic peak values.

Composition	Ratio (w/w)	Exothermic peak values (°C)	Endothermic peak values (°C)
PETN	Neat	212	142
OA	Neat	-	103, 192
PETN and OA	5:1	168, 212	102, 143
PETN and OA	5:2	127, 163, 211	103
PETN and OA	5:3	128, 154	103
PETN and OA	5:4	130, 137	104
PETN and OA	1:1	130, 138	104

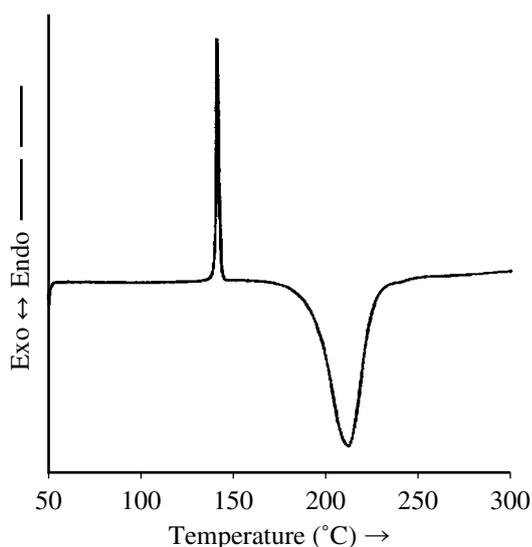


Fig. 1 DSC thermogram for PETN.

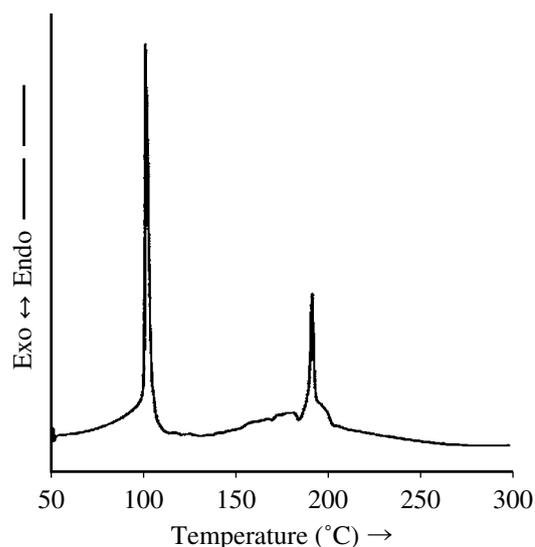


Fig. 2 DSC thermogram for Oxalic acid.

The DSC curve of neat PETN (Fig. 1) shows one endothermic peak at 142°C which is characteristic of its melting and one strong exothermic peak at 212°C which is due to its thermal decomposition⁸⁾. The DSC curve of neat OA (Fig. 2) shows two strong endothermic peaks, one at 103°C with onset at 100°C and the other one with onset at 190°C. The above observations are in agreement with the reported values of loss of water of crystallization of oxalic acid dihydrate (100°C – 105°C) and melting point of anhydrous OA (189.6°C)⁹⁾.

The DSC curve of PETN and OA in the ratio of 5:1 (Fig. 3) exhibits two endothermic peaks; one at 102°C and the other at 143°C representing the dehydration of OA and melting of PETN respectively. It also exhibits two exothermic peaks at 168°C and 212°C. The first exotherm could

be attributed to the sensitized decomposition of PETN due to the presence of OA and the one at 212°C is of residual PETN.

The DSC curves of PETN-OA in the ratio of 5:2, 5:3, 5:4 and 1:1 (Figs. 4 – 7) show strong endothermic peaks at peak temperatures 103°C, 103°C, 104°C and 104°C respectively which could be due to the dehydration of OA. The mixture of 5:2 of PETN and OA shows three exotherms; at 127°C, at 163°C and at 211°C. The first exotherm could be attributed to the decomposition of Pentaerythritol trinitrate so formed due to the partial hydrolysis of PETN with H⁺ ions from oxalic acid. The proposed reaction could be;

The second exotherm could be attributed to the sensitized decomposition of PETN due to the presence of OA and the third exotherm indicates the presence of residual PETN.

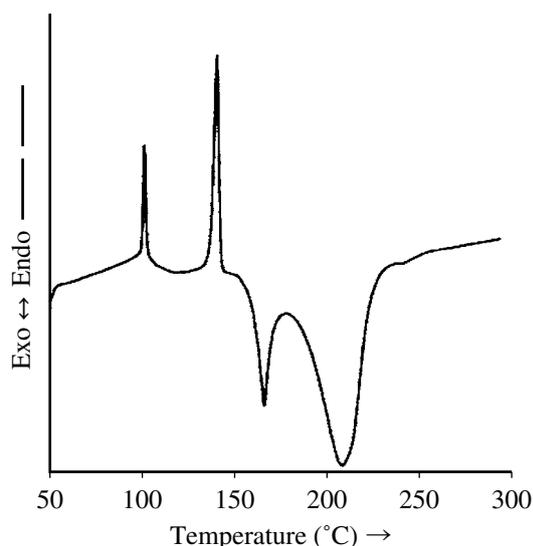


Fig. 3 DSC thermogram for the mixture of PETN and OA in the ratio of 5:1.

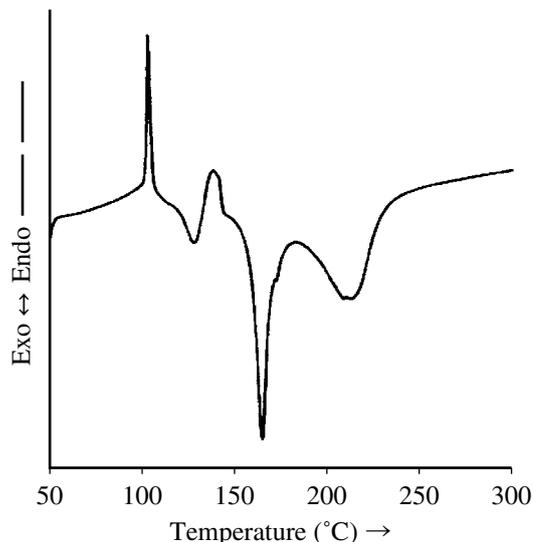


Fig. 4 DSC thermogram for the mixture of PETN and OA in the ratio of 5:2.

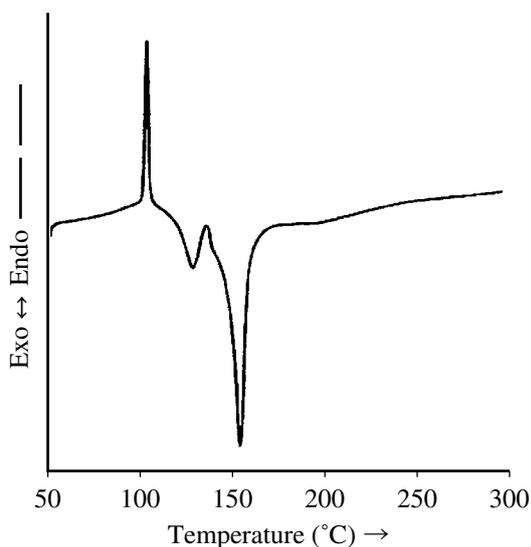


Fig. 5 DSC thermogram for the mixture of PETN and OA in the ratio of 5:3.

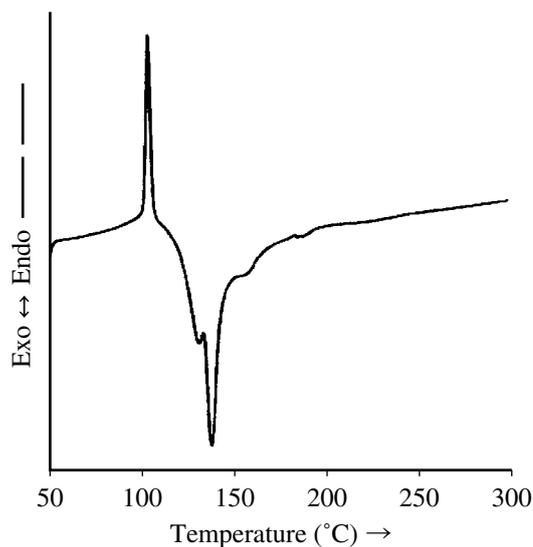
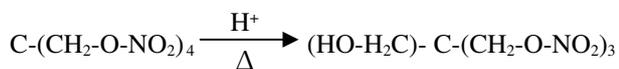


Fig. 6 DSC thermogram for the mixture of PETN and OA in the ratio of 5:4.



The DSC curve for the PETN-OA mixtures 5:3 and 5:4 shows double exotherm pattern having peak temperatures 128 °C & 154 °C and 130 °C & 137 °C respectively. The peak temperatures 128 °C and 130 °C could be due to the Pentaerythritol trinitrate formed and the peak temperatures 154 °C and 137 °C are due to the sensitized decomposition of PETN. No residual peak of PETN is observed in both the mixtures. This further shows that the sensitized decomposition of PETN in 5:4 ratio mixture occurs at a comparatively lower temperature than that of 5:3 mixture.

When the ratio of PETN and OA was incrementally changed from 5:4 onwards no appreciable deviation could be observed in the peak temperatures. Histograms

depicting the ratio of mixtures Vs peak temperature of the exothermic decomposition peaks of the sensitized decomposition of PETN and peak value of the Pentaerythritol trinitrate are plotted in (Fig. 8 and 9).

Figure 8 shows that, with the increase in the quantity of OA, there is a progressive and marked downward shift of peak temperature towards lower temperature region, which could be attributed to the sensitization of PETN. It is interesting to note that Fig. 9 shows no noticeable change in the peak decomposition temperature. This peak is missing in 5:1 mixture of PETN-OA suggesting that there is no formation of Pentaerythritol trinitrate taking place and only the sensitization of PETN occurs. The extent of thermolysis depends on the ratio of OA and hence the availability of protons.

All nitrate esters have one common mechanism by which

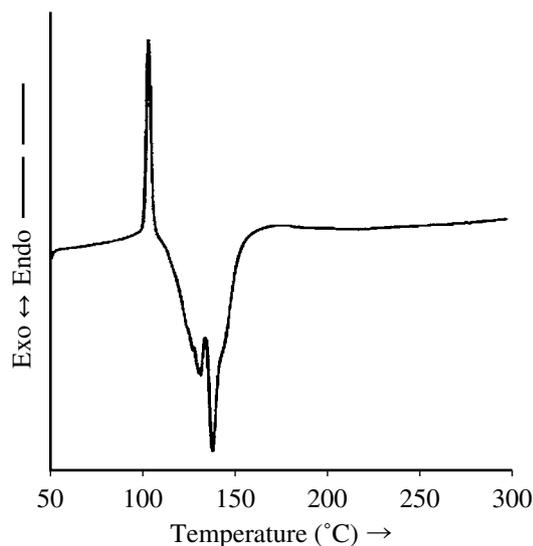


Fig. 7 DSC thermogram for the mixture of PETN and OA in the ratio of 1:1.

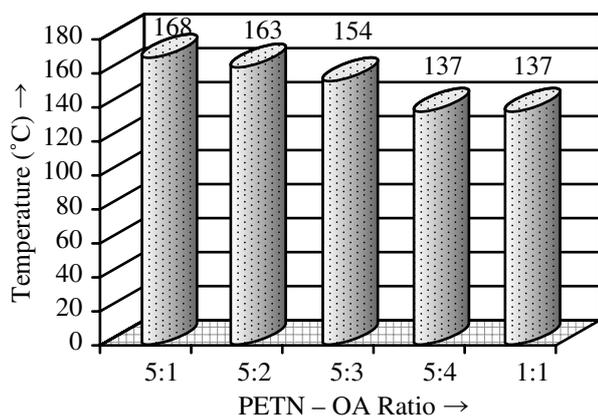


Fig. 8 Exothermic peak values of sensitized decomposition of PETN.

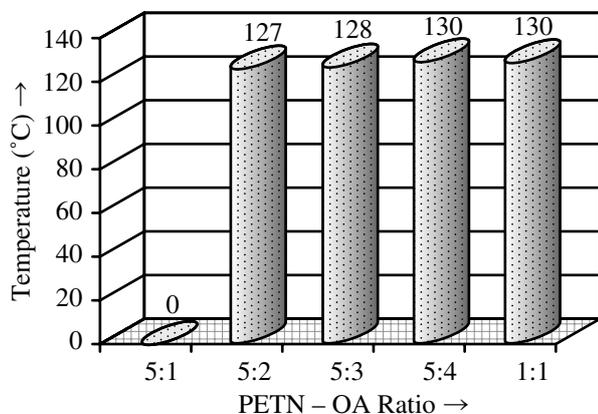


Fig. 9 Exothermic peak values of hydrolyzed product.

they decompose – homolysis of the X – NO₂ bond⁸). The credible explanation of lowering of decomposition temperature of PETN in presence of OA could be attributed to the formation of R-CH₂-O^{δ-}-NO₂^{δ+} type molecule thus facilitating an easy thermolysis of the bond, which leads to the decomposition of PETN at a temperature as low as 137°C, which is lower by 75°C than that of neat PETN.

4. Conclusion

Presence of Oxalic acid sensitizes PETN through the formation of R-CH₂-O^{δ-}-NO₂^{δ+} type molecule, thereby reducing the decomposition temperature considerably.

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References

- 1) G. Hussein and G.J. Reeds, *Fuels*, 74, 273 (1995).
- 2) G. Hussein and G.J. Reeds, *Prop., Explos., Pyrotech.*, 20, 74 (1995).
- 3) C. P. Constantinou, T. Mukundan, and M. M. Chaudri, *Phil. Trans. R. Soc. Lond., A* 339, 403 (1992).
- 4) C. P. Constantinou, and M. M. Chaudri, *J. Therm. Anal.*, 44, 1301 (1995).
- 5) M. D. Cook and P. J. Haskins, *Proc. Ninth Symposium on Detonation*, pp. 1027 – 1036 (1989).
- 6) P.S. Makashir and E.M. Kurian, *Prop., Explos., Pyrotech.*, 24, 260 (1999).
- 7) E. E. Kilmer, *J. Spacecr. Rockets*, 5, 1216 (1968).
- 8) J. A. Zukas and W. P. Walters, "Explosive Effects and Applications", pp. 375 – 376 (1998), Springer-Verlag, New York.
- 9) I. L. Finar, "Organic Chemistry, Vol 1, Sixth edition, p. 447 (2003), Pearson Education (Singapore) Pte. Ltd., Delhi, India.