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Studies on energetic compounds
Part 31. Thermolysis and kinetics of RDX and some of its plastic bonded explosives

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Abstract

Thermal analysis of RDX and its three plastic bonded explosives (PBXs) namely RXE 9505, RXE 9010 and RXV 9010 were done using various thermo analytical techniques, under different conditions. Although, the thermal analyses do not show any significant reduction in thermal stability of RDX, there are results, which suggest that the presence of binder alters the reaction pathways. Kinetic analysis of isothermal TG data was made by model fitting methods as well as a model free isoconversional method. The merits and demerits of both modes of kinetic approaches were evaluated critically. Conventional model fitting methods fail to describe the complex reactions during thermolysis of both RDX and its PBXs. Isoconversional method shows that the mechanisms of thermolysis of RDX and its PBXs are different, in the same temperature range. Role of binder was found to be in facilitating the reaction to take place in the condensed phase and reducing the role of competing reaction channels such as evaporation and gas phase thermolysis. Rapid thermolysis of the samples was studied by measuring ignition delay and evaluating its kinetic parameters.

Keywords: Plastic bonded explosives; RDX; Thermolysis; Kinetics; Isoconversional method

1. Introduction

PBX is a composite energetic material (CEM), which contains an energetic compound as filler in a polymer (binder) matrix. The basic aim of coating an energetic compound with a polymer binder is to reduce its sensitivity and give mechanical strength for shaped explosive charges. Pressing is made easier in PBX moulding powders and thus the higher density helps to attain better performance. Thermal analysis is an integral part of research and development of high energetic materials (HEMs) due to obvious reasons. Initiation by most of the hazardous stimuli such as shock, impact, spark, etc., is believed to be triggered off by the thermal event produced [1]. Moreover, thermal decomposition mechanisms and products influence the performance of HEMs. Thus deep understanding of various physico-chemical processes that are occurring during thermolysis of HEMs is required for performance prediction and safety evaluation.

Thermal behavior of PBXs may be different from that of pure energetic compound because the binder as well as other additives such as plasticiser may influence the thermo chemistry. In fact studies on composite solid propellants, which are essentially similar in composition to that of PBXs show that binder plays a vital role in their thermolysis and combustion. For example, Oyumi et al. [2] showed that presence of bis(azidomethyl)oxetane/tetrahydrofuran (BAMO), which is a copolymer binder, initiated and accelerated the rate of HMX thermal decomposition in their composite propellant. Bazaki et al. [3] have investigated the effect of chemical nature of binder on burning rate characteristics of ammonium perchlorate (AP) based composite propellants. They have concluded

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that burning rate appears to be very much dependent on the type of binder used. However, the role of binder in thermolysis of PBXs is less explored [4] and meagerly available in open literature. Various establishments involved in formulation of PBXs have reported some routine characterization of PBXs [5–9]. But these are inadequate to understand the effect of binder on thermal stability of the energetic filler and the underlying thermo chemistry. Thus, some systematic thermal studies on various PBX formulations have been initiated in this laboratory. Thermal analysis and kinetics thereof on RDX–HTPB PBX, showed that the thermolysis pathways are different in pure RDX and the PBX [4,10]. Our recent studies [11] showed that thermal stability of HMX decreases when it is coated with Estane and extent of lowering increases as the percentage of binder increases. Thus, it was found interesting to study the role of Estane during thermolysis of its PBX with RDX. The effect of Viton A, which is thermally more stable than Estane has also been investigated and the results are presented here.

There are a number of correlations available in literature between kinetics of thermolysis in HEMs and performance parameters. Cook et al. [12,13] proposed that the kinetics of initial reactions are important in determining detonation velocity. Zeman et al. correlated thermal decomposition kinetics of polynitroaromatic explosives at lower temperature with molecular structure [14], heat of explosion [15], detonation characteristics [14,16], and thermal stability [17]. The Arrhenius parameters are related to critical temperature of thermal explosion by Frank-Kamenetski model [18]. Thus it is important to assess the kinetic parameters for thermolysis of HEMs. Traditionally, model-fitting [19,20] approaches are used for evaluating global activation energy and pre-exponential factor. However, thermolysis of energetic materials is highly complex and is an intricate interplay of various physico-chemical processes. The individual steps may have different activation energies and contribution of individual steps to overall process may be a function of both temperature as well as extent of conversion. Such changes are not detected by traditional model fitting methods [21,22]. Recently the use of isoconversional methods is suggested as a solution for this problem [23,24]. We have used both traditional methods as well as a standard isoconversional method [25], for evaluating kinetic parameters for isothermal TG data of RDX and its PBXs. The Arrhenius parameters obtained using both methods have been compared critically.

2. Experimental section

Samples of RDX, Estane, Viton A and their PBX formulations containing RDX and Estane in the ratios 95:5 (RXE 9505), 90:10 (RXE 9010) and a RDX-Viton A PBX in the ratio 90:10 (RXV 9010) were supplied by TBRL, Chandigarh. These samples were used as received. Non-isothermal TG-DTG analyses of the samples were done by using a DuPont 2100 TG instrument at a heating rate of 10 °C min^{-1} (sample mass ≈5 mg, atmosphere = flowing N_2 gas at a rate of 60 mL min^{-1}). DSC thermal curves on the samples in open aluminium pans were collected by using DuPont 2100 DSC instrument at a heating rate of 10 °C min^{-1} (sample mass ≈2 mg, atmosphere = flowing N_2 gas at a rate of 60 mL min^{-1}). Non-isothermal TG-DSC analyses on the samples were made on NETZSCH STA 409 at a heating rate of 10 °C min^{-1} under flowing N_2 (60 mL min^{-1}) in an alumina crucible with a lid having small (pin size) hole in the centre. Non-isothermal TG analyses were also made in static air atmosphere at a heating rate of 10 °C min^{-1}, using an indigenously fabricated TG apparatus [26] (sample mass ≈25 mg). DTA analyses of the samples were carried out in flowing air (60 mL min^{-1}) atmosphere at a heating rate of 10 °C min^{-1}, using a DTA apparatus by Universal Thermal Analysis Instruments, Mumbai. Sample mass was kept as ~5 mg for RDX and the PBXs. Isothermal TG studies of the samples were done at appropriate temperatures using the above stated indigenously fabricated TG apparatus under static air atmosphere. Approximately 25 mg sample mass has been used for each run. Measurements of ignition delay of RDX and the PBXs were made by tube furnace technique (TF) [27]. Details of the experiments were as reported earlier [28]. Thus all the experiments were in open condition, except in STA, where the analyses were made under partial confinement.

3. Results

3.1. TG-DTG and DSC

TG-DTG thermal curves of RDX, RXE 9505, RXE 9010, RXV 9010 and Viton A are given in Fig. 1 and the phenomenological data are summarized in Table 1. TG thermal curve of RDX exhibits mass loss in a single step, which approaches ~100%. Mass loss in Viton A takes place at very high temperature and its thermolysis occurs in a single step. TG and DSC thermal curves for pure Estane are not included, they are reported in our earlier paper [11]. TG-DTG thermal curves for PBXs differ from that of pure RDX in that there is an additional step of binder degradation, which follows the thermolysis of RDX in the first step. The second step in the case of Estane based PBXs is occurring in a wide range of temperatures. However, the second step for RXV 9010 is clearly distinct and the values of T_i, inflection temperature (T_s) and end-set temperature (T_f) for this step are given in Table 1.

DSC thermal curves are shown in Fig. 2 and the corresponding data are summarized in Table 1. Fig. 2 shows an endotherm followed by an exotherm for RDX and its PBXs. The initial sharp endothermic peak at ~206 °C is due to melting of RDX [29]. Enthalpy change (ΔH) during the exothermic decomposition of RDX and its PBXs is also calculated and given in Table 1. DSC thermal curve for Viton A does not show any process up to 400 °C, which is the upper tempera-