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STUDIES ON ENERGETIC COMPOUNDS

Part XXXIX. Thermal analysis of a plastic bonded explosive containing RDX and HTPB

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Thermal analysis of pure RDX and its plastic bonded explosive (PBX) with hydroxyl terminated polybutadiene (HTPB) has been undertaken using TG-DTG and DTA techniques. Isothermal TG has been done and the data therefrom has been used to evaluate kinetic parameters using model fitting method and a model free isoconversional method. Results of the work done are discussed briefly on a comparative basis by analysing the departure of the thermal behaviour of the PBX from that of RDX.

Keywords: *HTPB, isoconversional method, PBX, RDX, TA*

Introduction

Studies on thermal behaviors of energetic materials are an essential part of research and development in this area. This is in view of safety as well as performance parameters. Kinetic parameters and mechanistic aspects are highly useful for making predictions of performance parameters, for example 'shelf life' [1]. Thermal analysis of high energetic compounds is highly complex involving multi-steps and reactions in different phases. The scenario becomes much more complicated in composite energetic materials (CEMs), due to the presence of binder and other additives in addition to the energetic compound. Even the presence of very small amount of binder significantly alters or sometimes controls the mechanism of thermal decomposition in CEMs [2–9]. Among CEMs, studies on plastic bonded explosives are quite rare in open literature in comparison with composite propellants. Most of the studies reported on PBXs are either routine characterizations [10] or are not aimed at understanding the thermochemistry [11–13]. We have recently initiated an in-depth study to have a comprehensive idea of effect of various binders of PBXs. Thermal analysis of HMX takes place at a lower temperature in its PBXs with Estane as binder and the extent of lowering of decomposition temperature increases as the percentage of binder increases [14]. The role of binder was found to be in facilitating the condensed phase reactions and reducing the contribution of competing gas phase processes in PBXs of RDX with Estane and Viton A [15]. Even thermally stable, inert polymer such as Viton A and Kel F affect thermal stability of keto-RDX (K-6) to some extent, during a dynamic heating programme [16]. In continuation to these studies, thermal analysis of a PBX formulation containing RDX and HTPB has been carried out and the results are presented here.

Kinetic parameters of energetic materials are usually correlated with performance. But in recent times stress is being given to isoconversional methods [17, 18], over conventional model fitting methods, for obtaining kinetic parameters from thermoanalytical data. We have also compared [14–16] the merits and de-merits of both the approaches in thermal analysis of PBXs and found that isoconversional method has an edge over the conventional method, in describing the mechanism. The above stated kinetic approach is extended in the present study also.

Experimental

The PBX containing 85% (by mass) RDX and rest isophorone diisocyanate (IPDI) cured HTPB (here after will be named as HTRX 8515) and RDX were supplied by High Energy Material Research Laboratory (HEMRL), Pune. The samples were used as received. TG-DTG studies on HTRX 8515 and pure RDX (sample mass=2 mg, heating rate=10°C min^{-1}, N_2 atmosphere) have been undertaken at National Institute of Pharmaceutical Education and Research (NIPER), Chandigarh. The corresponding thermal curves are shown in Fig. 1 and the phenomenological data are summarized in Table 1. Non-isothermal TG on RDX and HTRX 8515 have been done using an indigenously fab-

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Table 1 TG and DTA data of RDX and HTRX 8515

Sample	TG data				Peak temperature/°C	
	T_i/°C		T_f/°C			
	air	N_2	air	N_2	air (DTA)	N_2 (DTG)
RDX	205	214	235*	256	239	239.5
HTRX 8515	205	215	214*	226	215	223.4

*Temperature at which the thermal ignition occurs

ricated TG apparatus [19] in our laboratory (Heating rate=10°C min^{-1}, sample mass≈25 mg and static air atmosphere). TG curves are shown in Fig. 2 and data are summarized in Table 1. Differential thermal analysis (Universal Thermal Analytical Instruments, Mumbai) has been carried out on RDX and HTRX 8515 (Heating rate 10°C min^{-1}, sample mass≈5 mg, static air atmosphere). The DTA curves are shown in Fig. 3 and the corresponding data are summarized in Table 1. Isothermal TG studies on RDX and HTRX 8515 have been undertaken in the previously stated indigenously fabricated TG apparatus (sample mass≈25 mg, static air atmosphere) at temperatures 220, 225, 230, 235 and 240°C (for RDX) and 195, 200, 205, 210 and 215°C (for HTRX 8515). The isothermal TG curves for HTRX 8515 is shown in Fig. 4 and that for RDX is reported elsewhere [15].

Kinetic analysis

Model fitting method

Kinetics of thermally stimulated reactions in solids is usually studied using the following equation

$$d\alpha/dt=k(T)f(\alpha) \tag{1}$$

where α is the extent of conversion, *t* represents time, *T* is absolute temperature, $k(T)$ is the temperature-dependent rate constant and $f(\alpha)$ is a function called the reaction model. The temperature dependency of rate constant is assumed to obey Arrhenius expression,

$$k(T)=A\exp(-E/RT) \tag{2}$$

where *A* is pre-exponential (Arrhenius) factor, *E* activation energy and *R* gas constant. Equation (1) is often used in its integral form, which for isothermal conditions becomes

$$g(\alpha)\equiv\int_0^\alpha[f(\alpha)]^{-1}d\alpha=k(T)t \tag{3}$$

where $g(\alpha)$ is the integrated form of the reaction model. Substituting a particular reaction model into Eq. (3) results in evaluating the corresponding rate constant, which is found from the slope of the plot of $g(\alpha)$ *vs.* *t*. For each reaction model selected, the rate constants are evaluated at several temperatures and the Arrhenius parameters are evaluated using the Arrhenius equation in its logarithmic form.

$$\ln k(T)=\ln A-E/RT \tag{4}$$

Arrhenius parameters were evaluated for the isothermal TG data (α=0–1) of HTRX 8515 and are reported in Table 2 along with correlation coefficient (*r*) for each model.

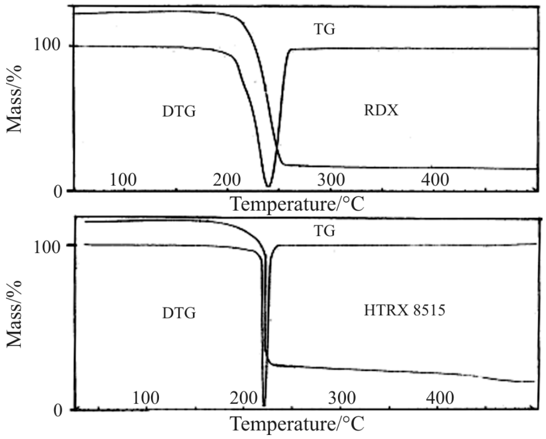

Fig. 1 TG-DTG curves of RDX and HTRX 8515 under nitrogen atmosphere

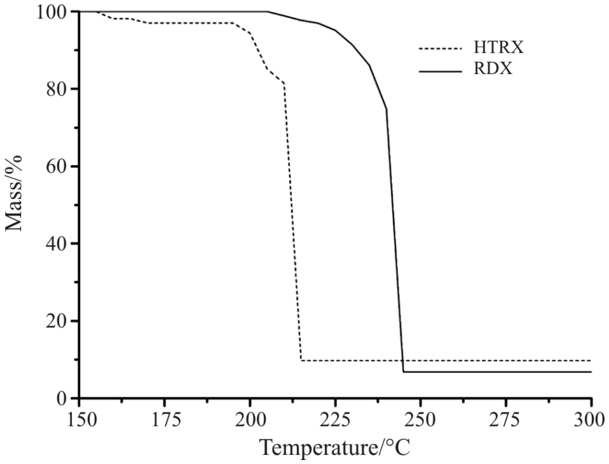

Fig. 2 Non-isothermal TG curves of RDX and HTRX 8515 in air atmosphere

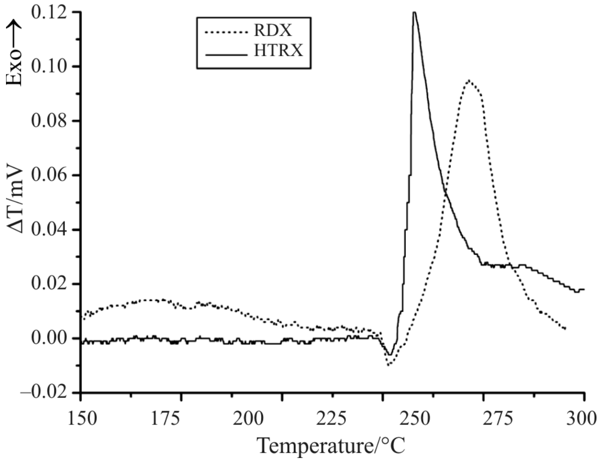

Fig. 3 DTA curves of RDX and HTRX 8515 under air atmosphere

Isoconversional method

In isoconversional method, it is assumed that the reaction model in Eq. (1) is not dependent on temperature. Under isothermal conditions, we may combine Eqs (3) and (4) to get,

$$-\ln t_{\alpha,\mathrm{i}}=\ln[A/g(\alpha)]-E_{\alpha}/RT_{\mathrm{i}} \qquad (5)$$

where E_α is evaluated from the slope for the plot of $-\ln t_{\alpha,\mathrm{i}}$ *vs.* T_{i}^{-1}. Thus values of E_α for RDX and its HTRX 8515 were evaluated at various α_{i}. The dependencies of activation energy (E_α) on extent of conversion (α) are given in Fig. 5.

Results and discussion

TG-DTG curves shown in Fig. 1 and the phenomenological data summarised in Table 1 show that thermal decomposition reaction of HTRX 8515 is considerably faster than that of pure RDX. The DTG peak temperature was observed at a lower temperature in the case of HTRX 8515, when compared to that of RDX. However the initial decomposition temperature (T_{i}) is same for both RDX and HTRX 8515. The non-isothermal TG data (Fig. 2 and Table 1) as well as DTA results (Fig. 3 and Table 1) show that atmosphere has no considerable effect on the thermal behaviour of RDX and HTRX 8515. T_{i} is almost same in the case of RDX and HTRX 8515 in static air atmosphere also. The first endothermic peak in DTA curve, at around 206°C, is due to the melting of RDX [20]. The exothermic peak temperature for HTRX 8515 is at a lower temperature than that for RDX. Thus the thermal studies show that, although the onset temperature for RDX and HTRX 8515 remains the same, once the reaction sets in, it occurs at a faster rate in the case of HTRX 8515.

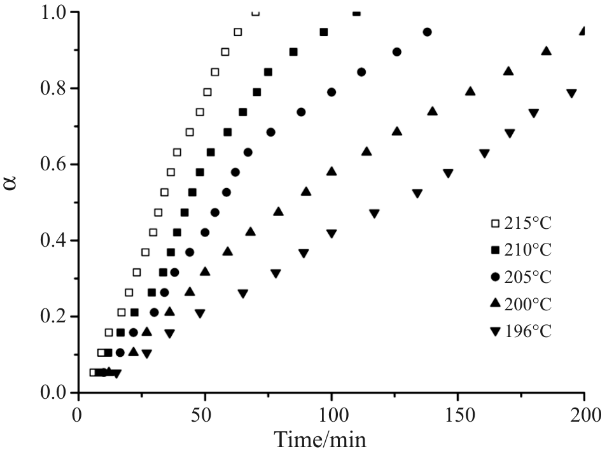

Fig. 4 Isothermal TG curves of HTRX 8515

All these results are in agreement with our earlier investigation on RDX based PBXs [15]. However, the major difference here is that, in those cases the binders used were thermally more stable than HTPB. The fastness in decomposition of HTRX 8515 may be due to the effect of exothermic decomposition of HTPB and the entrapment of the product gases from the early thermal decomposition of RDX, in the polymer matrix, which undergo secondary reactions in the gas phase. It is reported in [21] that HTPB has a two-step exothermic decomposition immediately followed by an endotherm. The IPDI cured HTPB urethanes also undergo two-stage decomposition with the DTA curve showing an initial exothermic peak followed by an endothermic peak [22]. Starting decomposition temperature as seen from TG, for HTPB urethane is around 250°C. However the exothermic processes during the first stage starts even before this temperature [21]. In the case of HTRX 8515, the stage-1 decomposition of HTPB seems to be combined with the decomposition of RDX. HTPB undergoes further decomposition (Stage 2) in the temperature range approximately 400–500°C which is exothermic in nature followed by an endothermic volatilization of the products of decomposition. In the case of HTRX 8515, the stage 2 decomposition of HTPB also occurs to a considerable extent due to the highly exothermic ignition of RDX. Thus it is also possible that the species evolving during the decomposition of HTPB interact chemically with the products of decomposition of RDX and thus the mechanism of decomposition may be different for the PBX from that of the pure compounds. But to check whether there is any change in mechanism, further studies are required. Analysis of the kinetic parameters for the decomposition process may give further insights into the complex thermochemistry. In order to determine the kinetic parameters for these compounds, isothermal TG curves were recorded and this data show that ther-

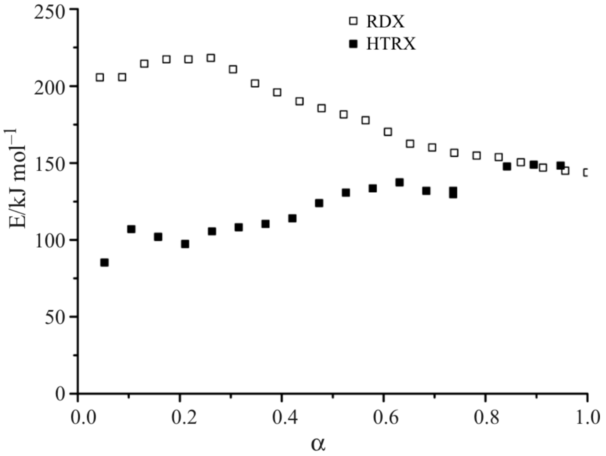

Fig. 5 Dependencies of activation energy on extent of conversion for RDX and HTRX 8515

mal decomposition reaction occurs at lower temperatures for HTRX 8515 in comparison with pure RDX.

We have already reported the kinetic parameters for decomposition of RDX elsewhere [15]. We observed that values of correlation coefficient can not be used to choose the best fit model. The same is true for the isothermal TG data of HTRX 8515 also. There are different models having same or very close values of r. The values of activation energy are almost same irrespective of the model used. Thus, an average value of ~143 kJ mol^{-1} was obtained for HTRX 8515. For RDX we have reported ~157 kJ mol^{-1}, as activation energy [15]. Thus the kinetic parameters obtained from model fitting methods indicate that there is a difference in mechanism of decomposition of RDX and HTRX 8515. However, we have observed earlier that the mechanism of decomposition for RDX is not very simple and can not be described by a global value of activation energy [15].

The values of activation energy for thermal decomposition obtained by the isoconversional approach, as shown in Fig. 5, clearly show that the mechanism of decomposition is different for RDX and HTRX 8515, at least in the initial stages of decomposition. In the case of RDX, initially activation energy of ~200 kJ mol^{-1} has been observed, which gradually changes into ~150 kJ mol^{-1}, at the final stages. Whereas, for HTRX 8515, activation energy of ~100 kJ mol^{-1}, has been observed during the initial stages, which gradually increases up to 150 kJ mol^{-1}. This result is different from that obtained for other PBXs of RDX [15]. In those cases the E_α was almost constant at ~200 kJ mol^{-1} which we assigned for condensed phase decomposition. The role of binder was found to be in facilitating condensed phase reactions. A detailed study on the decomposition of RDX and the kinetic parameters for the various reaction channels was reported by Long *et al.* [23]. Our results for the decomposition of RDX are similar to their results for a closed pan DSC experiment. Thus the initial stages of decomposition of RDX, is dominated by decomposition in the liquid state whereas gas phase decomposition takes over the final stage. The activation energy of 100 kJ mol^{-1}, during the initial stages of decomposition of HTRX 8515 may correspond to the heat of vaporization of RDX and/or complex interactions of binder decomposition products and RDX and/or its decomposition products. Moreover it may be fairly inferred that the final stages of PBX decomposition, is dominated by gas phase decomposition of RDX. Thus it can be seen that the faster rate of decomposition of the PBX, is due to the complex thermochemistry of binder/RDX decomposition which occurs with a lower value of activation energy.

Conclusions

The binder i.e. HTPB plays a vital role in the thermal decomposition of RDX in HTRX 8515. The thermal decomposition of HTRX 8515 occurs at a faster rate than that of RDX and the peak temperature in DTA as well as DTG has been considerably lowered in the PBX. Mechanism of thermal decomposition for RDX and HTRX 8515 is different, with differing activation energies.

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