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# Studies on energetic compounds
# Part 33: thermolysis of keto-RDX and its plastic bonded explosives containing thermally stable polymers

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**Abstract**

Thermolysis of keto-RDX (K-6) and its plastic bonded explosives (PBXs) containing Kel F and Viton A was studied using various thermo-analytical techniques. The PBXs decompose at slightly lower temperatures than K-6 with higher heat release. Kinetic analysis of isothermal TG data was done by using both model fitting methods and a model free isoconversional method. Model fitting methods gave nearly same values of activation energy for all the samples. But the model free isoconversional method showed that the activation energy is dependant on extent of conversion and different values were obtained for thermolysis of K-6 and PBXs. The value of activation energy converged to a limit above $\alpha \approx 0.75$. This limiting value was close to the activation energy obtained by model fitting methods. Rapid thermolysis of the samples was studied using ignition delay measurements and deriving kinetic parameters out of the data. Activation energy for thermal ignition was nearly the same for all the samples.
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*Keywords:* Plastic bonded explosives; Keto-RDX; Thermolysis; Kinetics; Model-free isoconversional method

## 1. Introduction

2-Oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6) is a cyclic dinitrourea derivative and is the keto-derivative of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). K-6 is an interesting high explosive as it has high density ($\rho = 1.93\,\mathrm{g\,cm^{-3}}$) [1] and high heat of formation ($-41.9 \pm 4.2\,\mathrm{kJ\,mol^{-1}}$) [2]. The compound can be prepared from cheap starting materials and has 4% more energy than 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) at early volume expansions [2]. It also finds application as a fuel component in inflatable vehicle occupant protection device with reduced smoke [3]. However, the compound is more sensitive to impact than RDX [4], HMX [2] and is thermally less stable than RDX [4]. The sensitivity of energetic compounds to hazardous stimuli may be reduced by thoroughly coating them with thermoplastic polymers to make PBXs [5]. The function of the binder is to protect the explosive crystals from quick initiation due to external stimuli. The thin coating layer of polymers can absorb accidental energy pulses and distribute them evenly over the volume of the PBX, thereby preventing local decomposition and initiation. Another important function of the binder is to provide mechanical strength to shaped explosive charges. Thus, Mitchell et al. [2] have coated K-6 with 5% Viton A to form a PBX named RX-41-AB and small scale safety tests revealed that slight reduction in sensitivity to drop hammer impact and electric spark was achieved by coating.

Our interest in thermolysis of PBXs arises from the fact that a systematic study on this aspect is found rarely in the

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open literature [6]. Most of the studies reported on PBXs are either routine characterizations [7] or are not aimed at understanding the thermo-chemistry [8–10]. Thus, these studies are insufficient to understand the effect of coating on thermal decomposition mechanism and kinetics of the energetic compound in PBXs. Thermal decomposition pathways and the products influence the performance of any high energetic material (HEM). Moreover, studies on nitramine propellants [11–16] show that the binder plays a significant role during thermolysis. Our recent studies showed that the binder (hydroxyl terminated polybutadiene-HTPB) influences the thermolysis of RDX, in its PBX [17]. The thermolysis 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 percentage of binder increases [18]. 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 [19]. In a continuation of these studies, the thermolysis of K-6 and its four PBX formulations has been undertaken using various thermo-analytical techniques and the results are presented here.

In the literature, there are a number of correlations available between thermal decomposition kinetics and safety [20,21] as well as performance parameters [22–25]. Tompa and Boswell [9] reported that in some of the methods that are used by US Navy to qualify the performance and safety of munitions, they use the kinetic parameters for thermolysis to make predictions. Kinetic parameters for heterogeneous thermolysis reactions are conventionally determined using model fitting methods, which involves fitting the experimental data to a suitable model, representing a single step process. However, thermally stimulated reactions in solids, especially when they are energetic compounds, involve many reaction channels and multiple phases. The contribution of an individual step to the overall rate may be a function of extent of conversion. A single value of 'global activation energy' obtained by model fitting approach may not adequately describe all the complex processes involved. Determining dependencies of activation energy on extent of conversion using isoconversional methods has been suggested recently to overcome the problem. Although there are many isoconversional methods [26–28], Vyazovkin [29] has developed a model free isoconversional method, which was successfully used to describe the thermolysis kinetics of energetic compounds such as RDX [30], HMX [31], 5-nitro-2,4-dihydro-3*H*-1,2,4-triazole-3-one (NTO) [32], ammonium perchlorate (AP) [33], ammonium nitrate (AN) [34], ammonium dinitramide (ADN) [35,36] etc. The same method was applied to evaluate kinetic parameters for composite energetic materials (CEMs) such as composite solid propellants [11,37] and plastic bonded explosives [17–19]. Isoconversional kinetic analysis on thermolysis of K-6 has not been reported yet and hence we used the above method to evaluate kinetic parameters for thermolysis of K-6 and its PBXs.

## 2. Experimental

Samples of K-6, its PBXs with Viton A in the mass (%) ratios 95:05 (K-6V 9505), 90:10 (K-6V 9010) and with Kel F in the ratios 95:05 (K-6K 9505) and 90:10 (K-6K 9010) were supplied by HEMRL, Pune. These samples were used as received. All the non-isothermal analyses were performed at a heating rate of 10 °C min$^{-1}$. TG-DTA experiments on the samples were done on a Mettler Toledo Star system under inert atmosphere (flowing $N_2$ at a rate of 100 mL min$^{-1}$, sample mass ~ 1–2 mg). Non-isothermal TG thermal curves in static air atmosphere were recorded on our indigenously fabricated TG apparatus [38] (sample mass ~ 25 mg). DTA thermal curves on the samples were recorded under flowing air atmosphere (100 mL min$^{-1}$) using an instrument supplied

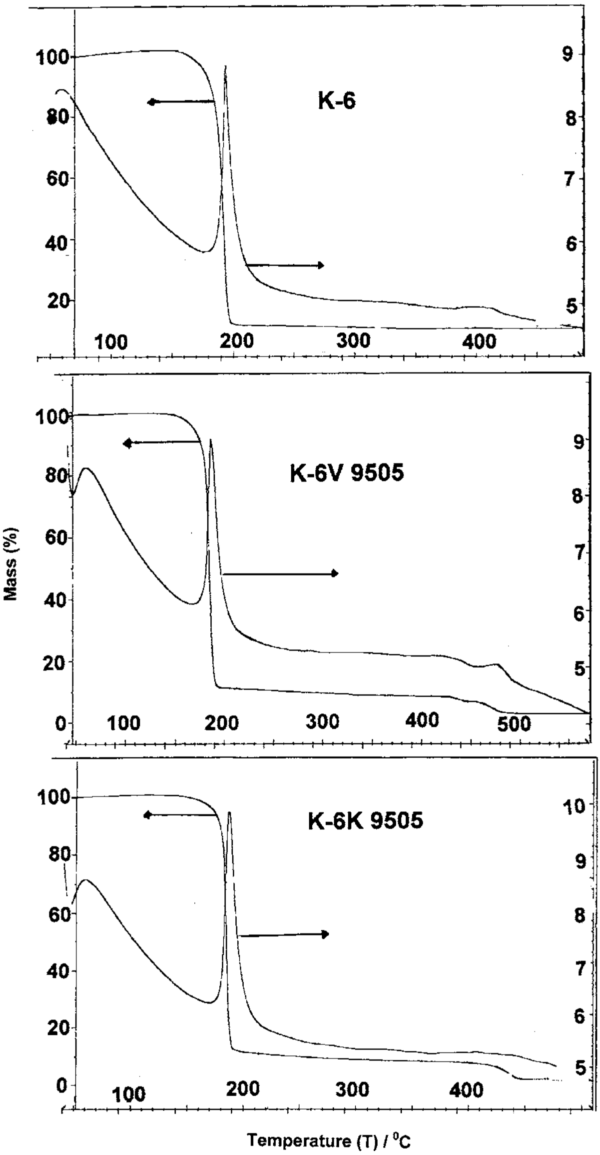

Fig. 1. TG-DTA thermograms recorded under inert atmosphere at a heating rate of 10 °C min$^{-1}$.

by Universal Thermal Analysis Instruments, Mumbai. DTA thermal curves for K-6 was recorded under vacuum and using a sealed DTA cup also. Isothermal TG thermal curves in the temperature range 170–180 °C were recorded using the above said indigenously fabricated TG apparatus under static air atmosphere (sample mass ∼ 25 mg). Ignition delay of the samples were measured using tube furnace (TF) technique [39,40].

## 3. Results

### 3.1. TG-DTA

The TG-DTA thermal curves of K-6, K-6K 9505 and K-6V 9505 are shown in Fig. 1. The thermal curves for K-6K 9505 and K-6V 9505 are representative in nature of that for K-6K 9010 and K-6V 9010, respectively, and hence the latter are not included. The corresponding phenomenological data of all the five samples are summarized in Table 1. Thermolysis of K-6 occurs in a single step with ∼90% mass loss. No further mass loss was observed for K-6 up to 500 °C. It is evident from Table 1 that the thermolysis of PBXs occurs in multi-steps. The first step in the thermolysis of PBXs is invariably the decomposition of K-6. Interestingly, the onset temperature ($T_i$), inflection temperature ($T_s$) and endset temperature ($T_f$) for the first step in the PBXs that are summarized in Table 1, have lower values than that for pure K-6. Kel F [41] and Viton A [19] are fluoro polymers and hence their thermolysis occurs at high temperatures. Thus, the mass loss above 400 °C for the PBXs is due to the thermolysis of binders in them.

Thermolysis of K-6 was observed in a single exothermic peak in DTA at ∼202 °C. The exothermic peaks corresponding to thermolysis of K-6 in the PBXs (Table 1) were observed at lower temperatures than that for pure K-6. A second exothermic peak was observed above 480 °C for PBXs with Viton A. However, for the PBXs with Kel F, there were no observable processes in DTA, after the first exothermic peak. Integral and normalized peak area of the samples for the DTA thermal curves is also reported in Table 1. For the PBXs, the integral area of the peaks was normalized according to the theoretical mass (%) of K-6 and the binder for their respective thermolysis processes.

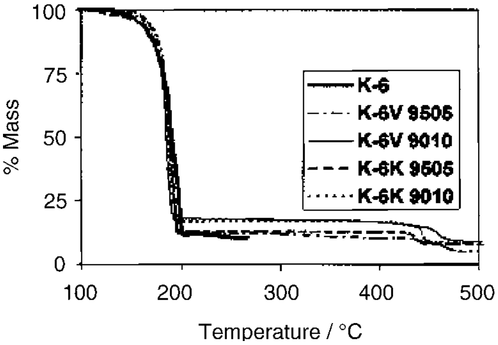

Fig. 2. Non-isothermal TG thermograms recorded under static air atmosphere at a heating rate of 10 °C min$^{-1}$. The respective lines represent each sample.

### 3.2. Non-isothermal TG and DTA in air atmosphere

To study the effect of atmosphere in the thermolysis of K-6 and its PBXs, non-isothermal TG was done in static air atmosphere and the corresponding thermal curves are shown in Fig. 2. The corresponding data profile is summarized in Table 2. Single step thermolysis of K-6 and multi-step thermolysis of PBXs were observed in these thermal curves also.

Table 1
TG-DTA phenomenological data on K-6 and the PBXs under inert atmosphere

| Sample name | TG | | | | DTA | |
|---|---|---|---|---|---|---|
| | $T_i$ (°C) | $T_s$ (°C) | $T_f$ (°C) | Percentage of mass loss | Exothermic peak temperature (°C) | Integral normalized peak area (°C$^2$ mg$^{-1}$) |
| K-6 | 191 | 199 | 203 | 89.6 | 202 | 183.2 |
| K-6V 9505 | 186 | 193 | 197 | 87.9 | 195 | 229.2 |
| | 434 | 440 | 449 | 1.5 | – | – |
| | 464 | 477 | 486 | 3.7 | 483 | 450.0 |
| K-6V 9010 | 185 | 193 | 195 | 83.2 | 193 | 214.5 |
| | 438 | 443 | 450 | 2.0 | – | – |
| | 470 | 483 | 492 | 7.8 | 488 | 397.6 |
| K-6K 9505 | 187 | 194 | 197 | 87.8 | 196 | 280.8 |
| | 426 | 441 | 448 | 5.7 | – | – |
| K-6K 9010 | 186 | 193 | 196 | 79.6 | 194 | 133.6 |
| | 413 | 418 | 426 | 3.6 | – | – |
| | 439 | 445 | 451 | 6.8 | – | – |

$T_i$: onset temperature; $T_s$: inflection temperature; $T_f$: endset temperature.

Table 2
TG and DTA phenomenological data of K-6 and its PBXs in air atmosphere

| Sample name | TG (static air) | | | DTA (flowing air) exothermic peak temperature (°C) |
|---|---|---|---|---|
| | SDT (°C) | FDT (°C) | Percentage of decomposed | |
| K-6 | 184 | 201 | 89.0 | 193 |
| Vacuum | – | – | – | 192 |
| Sealed | – | – | – | 196 |
| K-6V 9505 | 181 | 195 | 88.0 | 188 |
| K-6V 9010 | 180 | 192 | 81.7 | 186 |
| K-6K 9505 | 182 | 196 | 87.9 | 189 |
| K-6K 9010 | 179 | 195 | 82.0 | 186 |

SDT: starting decomposition temperature; FDT: final decomposition temperature.

DTA thermal curves recorded in flowing air atmosphere are given in Fig. 3 and the corresponding data is summarized in Table 2. The exothermic peak temperatures for K-6 and the PBXs (Table 2) had lower values than those observed under inert atmosphere. However, lowering of thermal stability of K-6 by the binders is observed in these thermal curves also.

### 3.3. Isothermal TG

Isothermal TG thermal curves on the samples were recorded at a narrow temperature range of 170–180 °C, because the thermal decomposition reaction is quite fast at higher temperatures and slow at lower temperatures. The thermal curve for K-6 is shown in Fig. 4 as a representative of all other samples. The thermal curves of all the samples have an induction period followed by an acceleration period, as the common feature.

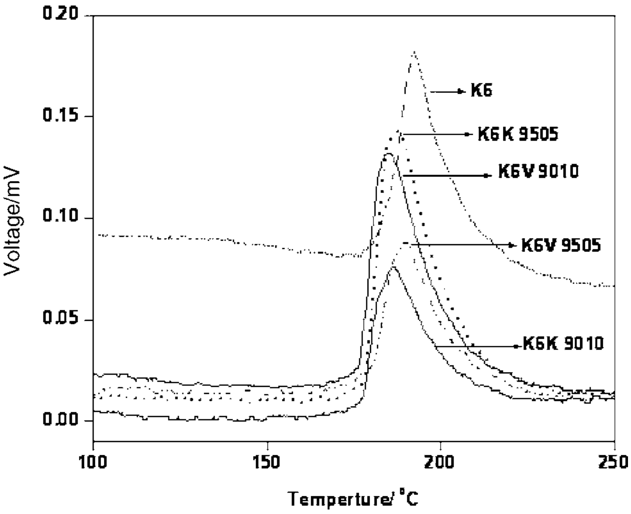

Fig. 3. DTA thermograms recorded under flowing air atmosphere at a heating rate of 10 °C min$^{-1}$. Lines differentiate the samples.

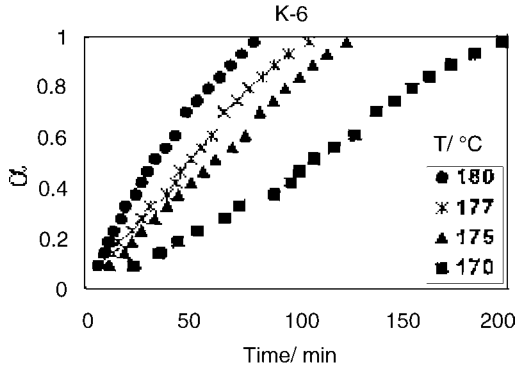

Fig. 4. Isothermal TG thermograms recorded under static air atmosphere. The temperature of the experiment (°C) is indicated by each symbol.

### 3.4. Kinetic analysis of isothermal TG data

#### 3.4.1. Model fitting method

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

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

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

$$k(T) = A\,\exp\left(\frac{-E}{RT}\right) \tag{2}$$

where $A$ is the preexponential (Arrhenius) factor, $E$ the activation energy and $R$ the gas constant. Eq. (1) is often used in its integral form, which for isothermal conditions becomes

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

where $g(\alpha)$ is the integrated form of the reaction model (Table 3). 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 $g(\alpha)$ versus $t$. 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.

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

Arrhenius parameters were evaluated for the isothermal TG data ($\alpha$ = 0–1) of all the samples. Correlation coefficient ($r$), that is sometimes used as a parameter for choosing the model giving best fit was also calculated for each model. We found that there are many models, which give same or very close values of $r$. Values of $E$ obtained from different models for a particular sample are nearly the same. This consistency

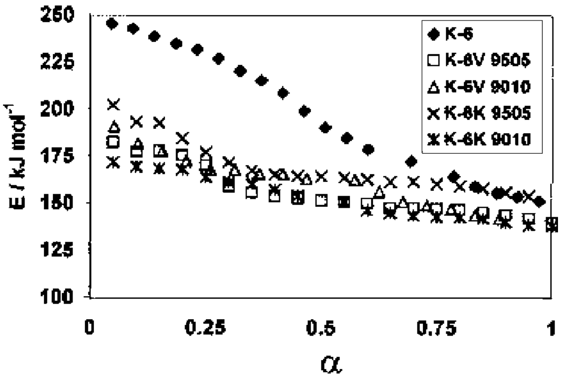

Fig. 5. Dependencies of activation energy ($E_\alpha$) on extent of conversion ($\alpha$) obtained from isoconversional method. Each sample is represented by respective symbols.

of activation energy is an advantage of isothermal methods. Thus, average values of 136.9 ± 7.6 kJ mol$^{-1}$, 135.3 ± 3.9 kJ mol$^{-1}$, 137.4 ± 3 kJ mol$^{-1}$, 143.8 ± 0.9 kJ mol$^{-1}$ and 130.3 ± 2.9 kJ mol$^{-1}$ were obtained as activation energies for the isothermal decomposition of K-6, K-6V 9505, K-6V 9010, K-6K 9505 and K-6K 9010, respectively in the temperature range of 170–180 °C.

### 3.4.2. Model-free isoconversional method

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

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

where $E_\alpha$ is evaluated from the slope for the plot of $-\ln t_{\alpha,\mathrm{i}}$ against $T_\mathrm{i}^{-1}$. Thus values of $E_\alpha$ for K-6 and its PBXs were evaluated at various $\alpha_\mathrm{i}$. The dependencies of activation energy ($E_\alpha$) on extent of conversion ($\alpha$) are given in Fig. 5.

### 3.5. Ignition delay measurements

Measurement of ignition delay ($t_\mathrm{id}$) at various temperatures for K-6 and the PBXs was done at high temperatures and the values are summarized in Table 3. The values of $t_\mathrm{id}$ fitted the following equation [42–44],

$$t_\mathrm{id} = A \exp\frac{E^*}{RT} \qquad (6)$$

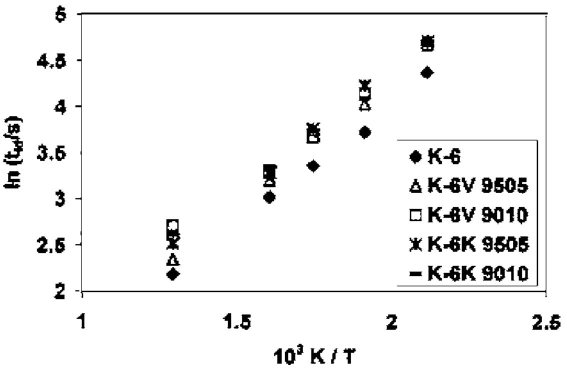

Fig. 6. Plot of natural logarithm of ignition delay ($t_\mathrm{id}$) against the reciprocal of the temperature ($T/K$) of measurement.

where $E^*$ is the activation energy for thermal explosion. Eq. (6) is used in its logarithmic form to evaluate $E^*$ from a plot of $\ln(t_\mathrm{id})$ against $T^{-1}$. The plot of $\ln(t_\mathrm{id})$ against $T^{-1}$ for K-6 and its PBXs are given in Fig. 6 and the values of $E^*$ are summarized in Table 3.

## 4. Discussion

The results of our thermal analyses on K-6 were similar to those reported in the literature [2,4]. Mitchel et al. [2] have reported an exotherm at 204.9 °C for K-6 as per DSC. Our result (202 °C) is close to this value. Ostmark et al. [4] have reported the occurrence of a strong exotherm having maximum at 195 °C according to DSC. This lower value is evidently due to the lower heating rate in their study, i.e. 5 °C min$^{-1}$. They [4] made a visual inspection, and reported that K-6 decomposes without melting. Mitchel et al. [2] have reported that crystalline K-6 melts at 184–185 °C, without mentioning the experimental method and there was no mention of any corresponding endothermic peak in their DSC study also. The visual inspection of Ostmark et al. [4] revealed that a gaseous bubble interacted with the solid and formed a liquid phase. In order to assess, the occurrence of any competing reaction channels, other than solid-state decomposition, DTA analyses of K-6 were done under various conditions. No endothermic process was observed in the thermal curves shown in Fig. 7 and the data summarized in Table 2 even under vacuum atmosphere (50 kPa). Thus, we could not observe sublimation or melting and hence it

Table 3
Ignition delay ($t_\mathrm{id}$), activation energy for thermal ignition ($E^*$) and correlation coefficient ($r$) for K-6 and the PBXs

| Sample | $t_\mathrm{id}$ (s) at temperatures (°C) | | | | | $E^*$(kJ mol$^{-1}$) | $r$ |
|---|---|---|---|---|---|---|---|
| | 200 | 250 | 300 | 350 | 500 | | |
| K-6 | 79.85 | 39.25 | 28.88 | 20.55 | 13.12 | 21.8 | 0.9984 |
| K-6V 9505 | 111.78 | 56.45 | 42.42 | 24.63 | 15.30 | 23.8 | 0.9968 |
| K-6V 9010 | 106.72 | 48.30 | 39.44 | 27.50 | 15.10 | 20.0 | 0.9962 |
| K-6K 9505 | 111.00 | 47.40 | 43.38 | 26.64 | 12.44 | 22.7 | 0.9983 |
| K-6K 9010 | 111.45 | 49.75 | 33.32 | 28.47 | 13.70 | 21.1 | 0.9985 |

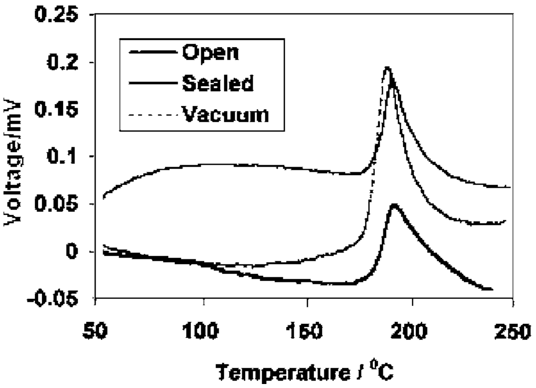

Fig. 7. DTA thermograms for K-6 under various conditions. Each condition is differentiated by separate lines.

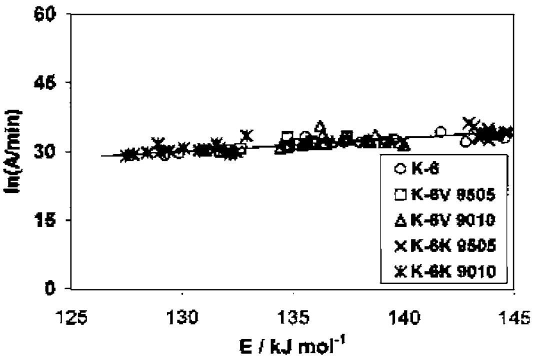

Fig. 8. Kinetic compensation effect observed for the kinetic parameters obtained from model-fitting approach. Samples are differentiated by symbols.

is reasonable to conclude that thermolysis of K-6 occurs in solid-state or in the condensed phase. However, when K-6 was confined by using a sealed DTA cup, the exothermic peak was observed at slightly higher temperature.

It is interesting to note that thermally stable polymeric binders lower thermal stability of K-6. Such a lowering was observed during DSC analysis of RX-41-AB by Mitchel et al. [2]. However, sensitivity of RX-41-AB was lower as compared to pure K-6, even when there was a slight decrease in thermal stability. Lower thermal stability of composite energetic material, compared with that of the corresponding pure energetic compound was reported earlier also [18,45] but binders in those cases were thermally less stable than the energetic compound. Binders in the present samples are fluoropolymers, which are chemically inert and they do not undergo thermal decomposition in the temperature range where thermolysis of K-6 occurs. Hence, the lowering in thermal stability cannot be attributed to any chemical interaction between the binder and K-6 or its decomposition products. There are probable physical reasons for the observed lowering of decomposition temperature for the PBXs. In K-6, cumulation of strong electronegative groups in the 1,2,3-positions leads to crowding and consequently a dipole is generated [1]. The dipole leads to stronger 'orientation interactions' and thus the crystal lattice is stabilised more and physical thermal stability is enhanced. In such cases where stabilizing influence of the crystal lattice is strong, even very small admixture of a solvent can markedly decrease thermal stability. It is known that Viton A and Kel F clearly dissolve nitramines at higher temperatures. For the PBX samples, lower thermal stability compared to K-6 may also be due to marked dissolution of K-6 in the binder matrix.

The integral normalized peak areas of DTA exotherms reported in Table 1 are in the following order, K-6K 9010 < K-6 < K-6V 9010 < K-6V 9505 < K-6K 9505. Higher heat release for the PBXs (except K-6K 9010) than K-6, show that the reaction pathways may be different. Lesser heat release for K-6K 9010 is associated with lesser mass loss (%) in the first step. Thus, the actual mass (%) of K-6 may be lower in K-6K 9010 than 90%.

### 4.1. Kinetic analysis

As suggested by recent studies [18,19,31], using the value of '$r$' as a statistical parameter to chose the 'best fit' model is questionable. The isothermal data fits well in mechanistically contrasting models and hence proposing mechanism based on model fitting method is also not reliable. Values of global activation energy obtained from model fitting methods is same for K-6 and the PBXs. A plot of all values of $E$ against corresponding $\ln(A)$ (Fig. 8) shows that all these values fall almost in a straight line obeying the following equation

$$\ln(A) = 0.274E - 5.36 \qquad (7)$$

Ostmark et al. [4] reported $280\,\mathrm{kJ\,mol^{-1}}$ as $E$ with a pre-exponential factor $7.0 \times 10^{29}\,\mathrm{s^{-1}}$ in the temperature interval 175–200 °C for thermolysis of K-6, using ASTM method E 698-79 from DSC studies. This pair of $E$ and $A$ also obey Eq. (7), indicating that our kinetic parameters are consistent with values reported by Ostmark et al. [4] using non-isothermal DSC and the difference in values are due to kinetic compensation effect.

The isoconversional analysis shows that thermal decomposition reactions of the samples are not simple as reflected by global activation energy from model fitting methods. K-6 has $E_\alpha$ values strongly dependent on values of $\alpha$. $E_\alpha$ decreases from an initial value of ~245 to ~150 kJ mol$^{-1}$ at $\alpha = 1$. However, the variation of $E_\alpha$ with $\alpha$ is not so drastic for the PBXs. All the four PBX samples have slightly different values of $E_\alpha$, but the nature of variation in $E_\alpha$ with respect to $\alpha$ is essentially the same. We can see from Fig. 5, that values of $E_\alpha$ are different for K-6 and its PBXs initially, but are approximately the same above $\alpha \approx 0.75$.

It has been evident from the above discussions that it is difficult to choose the best model solely from the value of $r$. Another approach to choose the best-fit model is plotting $\alpha$ against reduced time ($t/t_\alpha$), where $t_\alpha$ is the time required to reach a specified conversion. We have attempted this method also and found that no model can represent the thermal decomposition process in the full range of $\alpha$. Although the isoconversional method successfully describes the complex thermolysis of K-6 and its PBXs, it gives no direct mechanistic clue. The situation is trickier, when dealing with comparatively less explored material such as K-6, for which there are not much kinetic data available.

Since there is an induction period and the thermolysis is taking place in the solid-state, it may be possible that initial stages (induction period) are controlled by nucleation. The acceleration period may be controlled by nuclei growth. The process of nucleation is extremely sensitive to the prehistory of a solid. Thus, pure K-6 and K-6 in the PBXs may have different prehistory and hence the difference in activation energy for nucleation. In the molecular level, there are many reaction pathways possible for K-6, as for RDX, which is a closely related compound in structure. Ostmark et al. [4] studied the decomposition of K-6 and RDX, using mass spectrometry (MS), laser induced mass spectrometry (LI/MS), chemiluminescence and DSC. They have concluded that concerted symmetric fission of C–N bonds is less important for K-6 than for RDX. They suggested $NO_2$ elimination followed by a break down of the ring as the probable mechanism of decomposition of K-6. For the production of NO from K-6 by chemiluminescence in the temperature range 90–120 °C, activation energy of $140\,kJ\,mol^{-1}$ and a pre-exponential factor of $9 \times 10^9\,s^{-1}$ was obtained. In our study, $E_\alpha$ was $\sim 150\,kJ\,mol^{-1}$ above $\alpha > 0.75$ for K-6 and the PBXs and hence the final stages of thermolysis may be limited by breaking of $N{-}NO_2$ bond. Ostmark et al. [4] have calculated bond breaking energies for $N{-}NO_2$ and concerted triple fission (C–N) of RDX and K-6, using modified neglect of diatomic overlap (MNDO) using PM3 parameter set at the unrestricted Hartree–Fock (UHF) level of theory. They have reported $\Delta H_{bond1} = 26.4\,kcal\,mol^{-1}$ ($110.5\,kJ\,mol^{-1}$) and $\Delta H_{bond2} = 21.5\,kcal\,mol^{-1}$ ($90\,kJ\,mol^{-1}$) as bond scission energies for the two types of (non-equivalent) N–N bonds in K-6. The bond scission energy for concerted triple fission was calculated to be $\Delta H_{bond} = 67.1\,kcal\,mol^{-1}$ ($280\,kJ\,mol^{-1}$). But the values calculated for RDX, i.e. $\Delta H_{bond}$ for N–N $= 22\,kcal\,mol^{-1}$ ($92.1\,kJ\,mol^{-1}$) and $\Delta H_{bond}$ for concerted triple fission $= 68.2\,kcal\,mol^{-1}$ ($285.4\,kJ\,mol^{-1}$) were quite different from the experimental values ($\sim 200\,kJ\,mol^{-1}$) for the former [46,47] and $150\,kJ\,mol^{-1}$ for the latter [48,49] processes, respectively. If the calculated values of Ostmark et al. [4] are correct, then the initial stage of K-6 decomposition may be controlled by concerted triple fission and as the reaction progresses, the contribution from $N{-}NO_2$ bond breaking increases. In the PBXs the contribution from concerted triple fission is considerably less and the other process dominates preferentially at the final stages. Moreover, as stated previously dissolution of K-6 may take place in the binder matrix and thus in the solution phase $N{-}NO_2$ bond cleavage is promoted, which has lower activation energy. However, as there is an insufficiency of reliable data on kinetic parameters for K-6, the interpretations in the present study must be treated as indicative and not exhaustive.

Although, K-6 has higher heat of formation than HMX [2], it ignites and does not explode under conditions of rapid heating. The same was observed for HMX [19] and their PBXs also and was attributed to the less confined experimental conditions. K-6 has lower values of $t_{id}$ than the PBXs at the same temperatures. But the activation energy for thermal ignition was found to be almost same for K-6 and the PBXs. Lower value of $E^*$ shows that the ignition kinetics is not controlled by any molecular process. Heat transfer or mass transfer may be the rate controlling process during ignition. The higher value of $t_{id}$ for PBXs than K-6 is similar to lesser sensitivity of PBXs. Thus, the lower sensitivity of the PBXs may be due to better heat dissipation, which prevents local initiation, as observed during ignition delay measurement.

## 5. Conclusions

Even thermally stable, inert polymers such as Viton A and Kel F affect thermal stability of K-6 to some extent, during a dynamic heating programme, when they are used as binders to make the PBXs. The reason for this may be the marginal solubility of K-6 in the binder matrix. Conventional model fitting approach fails to describe any difference in mechanism of isothermal decomposition of K-6 and its PBXs. Moreover, these kinetic parameters suffer from kinetic compensation effect. Isoconversional analysis shows that the $E_\alpha$ varies as the reaction proceeds, for both K-6 and the PBXs and the variation is different for the pure compound and the PBXs. However, further studies are required to explain these changes in terms of mechanism. The rapid thermolysis of K-6 and its PBXs seems to follow the same route.

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