New Insights into Kinetics of PETN Decomposition from the Product and Reactant Point of View: An Investigation with Mass Spectrometry and Differential Scanning Calorimetry

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Abstract:

Pentaerythritol Tetranitrate (PETN) is a benchmark organic energetic material and is used in both military and industrial applications. Accurate kinetic parameters for the decomposition of energetic materials are required to predict the hazards, thermal cook-off and properties of PETN. Kinetic parameters of PETN decomposition have been previously reported in wide range of values. We are attempting to find new insights on the the kinetics of PETN decomposition by studying kinetics of gas evolution and heat released from the reaction. Gas evolution kinetics is studied by a mass spectrometer coupled with a thermogravimetric analyzer (TGA-MS) and heat released in the reaction with a differential scanning calorimeter (DSC) in open and closed pan. PETN single crystals are used as the samples. The activation energy of decomposition is obtained as a function of extent of reaction by the isoconversional kinetic analysis. The activation energy for the generation of NO₂ (m/z = 46) in PETN decomposition is consistent with the bond energy of RO–NO₂ in nitrate esters. The activation energy for the overall PETN decomposition is similar to that of the generation of NO₂. The effect of confinement on the decomposition kinetics in TGA-MS and DSC, are also discussed in this work. This investigation shows that activation energy for PETN decomposition is in the range of 170–176 kJ/mol.

Key Words: Kinetics, PETN, Decomposition, Mass Spectrometry

1. Introduction

Organic energetic materials (OEMs) with high energy density are extensively used in military warhead and mining industries. Application, storage, safe handling and shelf life of OEMs depend on the decomposition process due to the potential of sudden release of extreme heat and sudden expansion of volume of decomposition products [1]. Moreover, initial stages of detonation depend explicitly on the kinetics of decomposition [2]. Hence it is important to investigate the true kinetics of the thermal decomposition of OEMs – to predict the hazard, properties of these materials in long term storage, thermal cook-off, runaway, self-heating, and to design reactors and chemical processes for the production of these compounds [3–5]. Use of inaccurate parameters in predicting the kinetic and thermodynamic properties can cause serious accidents in synthesis, storage and application of OEMs [6–10].

A proper understanding of the decomposition of a benchmark OEM such as Pentaerythritol Tetranitrate (PETN) is required because of its wide applications as a component in propellants and main charges [11]. PETN is a very strong secondary explosive with a high heat of detonation of 1.5 kcal/gm [12]. It has similar physical and chemical properties to other OEMs. The molecular structure of PETN is shown in Figure 1(a).

A wide range of values, 125-293 kJ/mol, for the kinetic parameters such as activation energy for PETN decomposition has been previously reported in various studies [13–17]. Other investigations explained the possible pathways, and products, of PETN decomposition at various temperatures [18–20]. These studies also showed that the major gas phase components generated from the decomposition of PETN are nitrogen dioxide (NO_2), nitric oxide (NO), carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O). However, gas evolution kinetics resulting from thermal decomposition and its correlation with the safety, storage, handling, thermal cook-off,

initiation and detonation are least understood [3]. The kinetic parameters for each component of the decomposition products are required to develop better thermodynamic and kinetic models for the explanation of the behaviour of energetic materials upon thermal effect. A thermogravimetric analyser combined with a mass spectrometer (TGA-MS) is used for analysing the real-time gas phase products evolved from thermal decomposition [21–22], and can be used to obtain kinetic parameters of thermal decomposition [23]. Since TGA-MS and differential scanning calorimeter (DSC) studies of decomposition are conducted by studying two completely different parameters in two distinct types of confinements of samples, a combined study with these two experimental tools will add new insight into the kinetics of PETN decomposition.

The aim of this paper is to understand the non-isothermal reaction kinetics of PETN decomposition from the standpoint of evolved gaseous products and the heat released from the reaction. A single crystal of PETN was used as sample in each experiment. The gas phase products were non-isothermally observed in TGA-MS. To compare the gas evolution kinetics in PETN decomposition, the heat released in the reaction was studied with a DSC in closed and open pan. The activation energy for the evolution of a specific gas phase component, and for overall PETN decomposition, were obtained by the isoconversional kinetic analysis. The Kissinger-Akihara-Sunose (KAS) model was used for the isoconversional kinetic analysis [24].

2. Experimental

PETN powder (with a 99.99% purity) was obtained from Lawrence Livermore National Laboratory. PETN single crystals were grown by following the methods explained elsewhere [25]. Weight of the samples were around 5mg and thickness of the sample was around 1mm. Figure 1(b) shows a typical single crystal of PETN. Since samples are single crystal, and sample mass and thickness in the experiments are similar for all the experiments, the effect of particle size, mass and geometry has no effect on the results. Both the DSC (model-Q20) and TGA (model: Q50) were supplied by TA Instruments. The mass spectrometer (model: GSD 320) was obtained from Pfeiffer Vacuum Inc. Vacuum in the MS was maintained at $\sim 1 \times 10^{-6}$ mbar. Helium, with a purity of >99.99%, was used as a purge gas to minimize any gas phase reaction in TGA-MS. Helium is also passed through the absorption column to eliminate moisture and other impurities. In TGA, the balance purge gas flow rate and the sample purge gas flow rate were 10 mL/min and 90 mL/min, respectively. At these conditions, the time lag between gas evolution and detection in the MS did not influence the results significantly [26]. Experiments in TGA-MS and DSC were performed at the heating rates of 5, 10, 15 and 20 K/min.

3. RESULTS AND DISCUSSION

3.1 Kinetics of gas evolution from PETN decomposition

PETN decomposition is initiated with the hemolytic scission of O–NO₂ bond by releasing NO₂ as following equation:

The detail reaction mechanism of NO₂ release in gas phase is reported in the literature [17, 27]. In this investigation, the energy barrier for NO₂ production was experimentally obtained by observing the ion current at m/z=46 in MS. There are no other decomposition products reported in the literature at m/z=46 that can convolute the TGA-MS curve for NO₂. Figure 2 shows NO₂ evolution in the reaction as a function of temperature at various heating rates. The NO₂ generation increased with increasing temperature; after reaching a maximum value, NO₂ generation gradually decreases with increasing temperature. Comparison with the DSC curves, which are presented in Figure 3, shows that NO₂ generation is only happened after the melting point. In Figure 3 melting of PETN is appeared at temperature around 142 °C in the endothermic Peak which is consistent with the literature value [28, 29]. It also demonstrate that, because of using single crystal as sample, evaporation and autocatalysis is not affecting the kinetics of decomposition of PETN.

An isoconversional kinetic analysis of the TGA-MS data was conducted using the KAS model [24] for the first order decomposition

$$\ln \frac{\beta}{T_{\alpha}^2} = Constant - \frac{E_a}{RT_{\alpha}} \quad (2)$$

where β is the non-isothermal linear heating rate, E_a is the activation energy, $\alpha = \frac{A_{T_{\alpha}}}{A}$ where $A_{T_{\alpha}}$ is the area under the curve at any instantaneous temperature, T_{α} , and A is the total area under the curve. Here α indicates the cumulative fraction of the completed reaction at temperature T_{α} . The activation energy is calculated as a function of extent of reaction from the slope of the straight line of $\ln \frac{\beta}{T_{\alpha}^2}$ vs $1/T_{\alpha}$ plot.

Figure 4 showed the α for NO_2 generation in PETN decomposition as a function of temperature. T_{50} , which is the temperature (T_α) at the completion of 50% of a reaction, were obtained from Figure 4. In this work, T_{50} is considered as a characteristic temperature for the comparison of kinetics observed in TGA-MS and DSC. T_{50} for NO_2 production in TGA-MS was found to be at 188, 195.8, 199.5 and 201.5 °C at 5, 10, 15 and 20 K/min, respectively.

β and T at various values of α are fitted into equation 2 and plotted in Figure 5. Although a series of lines can be obtained for each value of α , only three of the curves are shown from both TGA-MS and DSC for clarity. The linearity of the fit with fitting parameter $R^2 \sim 0.99$ shows that NO_2 evolution from PETN decomposition follows similar reaction order at each α .

The activation barrier for the NO_2 generation in PETN decomposition as a function of α is obtained from the above analysis shown in Figure 6. The activation energy for the decomposition is similar in the entire range of α . Experimental values of activation energy for NO_2 release from PETN are found to be between 168 to 181 kJ/mol with an average activation energy of 175.8 kJ/mol. Figure 6 also shows that experimental value is consistent with the theoretical value of $\text{RO} - \text{NO}_2$ bond energy in nitrate ester that is 170.3 kJ/mol [14]. To the best of our knowledge, this is the first experimental demonstration of obtaining the activation energy of NO_2 generation from the decomposition of PETN.

The ion current for the component at $m/z=30$ was also observed in MS. Previous studies showed that both NO and CH_2O are decomposition products at $m/z=30$ [20]. A similar activation energy for this component was obtained as for the generation of NO_2 . The ion current for the component at $m/z=18$, which is most likely water (H_2O) since there are 8 hydrogen and 12 oxygen atoms in PETN structure, was also observed, and is shown in Figure 7. The activation energy of this component was obtained at 84 – 143 kJ/mol by analysing Figure 7 and shown in

Figure 6. Initially activation energy increase from $\alpha=0.1$ to $\alpha=0.3$, and then activation energy is almost constant at $\alpha>0.3$. The exact mechanism for the observed trend cannot be explained from this study but suggests that there may be multiple pathways for the evolution of water based on heating rate.

3.2 Isoconversional Kinetic Analysis of Heat Release in Reaction

The kinetics of NO_2 generation in PETN decomposition observed by TGA-MS is then compared with that of overall PETN decomposition investigated by studying the exothermic heat release in the reaction using a DSC. Figure 3 shows the DSC thermograms of PETN that are obtained by running the experiments in closed pan and open pan. Figure 4 compares the α from DSC experiment with that of TGA-MS at various heating rates. α in both experiments shifts to the right with increasing heating rate. For $\alpha = 0.5$, the T_{50} from DSC experiment shifts to 197.4, 204.3, 208.9 and 212.6 °C for the heating rate of 5, 10, 15 and 20 K/min, respectively. It is evident from Figure 4 that T_{50} in DSC experiment is around 10 °C higher compared to the T_{50} in TGA-MS experiment. Figure 4 also shows that differences of the decomposition temperature in DSC and TGA-MS increase with the increasing temperature. This effect may be due to the confinement of the sample because the samples in DSC is run in crimped pan; on the other hand samples in TGA-MS are run in open pan. To test this hypothesis, experiments with open pans are also conducted in DSC that are shown in Figure 3. Comparison of α in Figure 4 shows that T_{50} for open pan DSC is much closer to the results of TGA-MS. Moreover, T_α for NO_2 generation and decomposition of PETN in open pan DSC is even closer at lower value of α ($\alpha<0.3$). At this range of α , difference in T_α at these values of α can be mainly attributed to evaporation of samples in an open pan.

Figure 5 compares the KAS plots ($\ln \frac{\beta}{T_\alpha^2}$ vs $1/T_\alpha$) of NO₂ generation with that of overall PETN decomposition in open and closed pan. As mentioned earlier, only the plot at $\alpha=0.1$, 0.50 and 0.70 are shown for clarity of the Figure 5. These curves qualitatively compares kinetics of the decomposition. NO₂ gas evolution and overall PETN decomposition kinetics in closed and open pan shows identical linear behavior following a similar reaction order at all values of α ; although the slope of the curve for PETN decomposition in open pan at $\alpha=0.5$ is different from the other two which indicates a different activation energy at this condition. Figure 5 also demonstrate that, for PETN decomposition, the order of reaction is not influenced by the confinement of samples. At $\alpha=0.1$, KAS plot for NO₂ generation and decomposition in open pan is almost similar showing a similar slope and intersection.

Figure 6 compares activation energy, as a function of extent of reaction, of NO₂ generation with that of overall PETN decomposition in closed and open pan. The activation energy for overall decomposition studied in closed pan is almost constant in the whole range of α , and the average value of activation energy is 170 kJ/mol. As shown in Figure 6, this result is consistent with the activation energy for the scission of NO₂ group from the PETN structure observed in TGA-MS. Activation energy for the decomposition of PETN obtained from open pan experiment is also shown in Figure 6, which shows that the activation energy at $\alpha=0.1$ from open pan experiment is almost same with the activation energy obtained from closed pan experiment and also with that of NO₂ generation. At $\alpha>0.2$, activation energy obtained from open pan experiment is lower compared to that of closed pan as well as the activation energy of NO₂ generation. At these value of α , heat released per unit mass of sample is not accurately observed

in open pan experiments as the Figure 2 shows that heat release in open pan is less than that in closed pan; moreover evaporation of PETN will be high and can convolute the decomposition kinetics which cause a faster decomposition with low activation energy.

However, kinetics of decomposition investigated by the DSC and the TGA-MS showed that decomposition of PETN might be limited by the scission of NO₂ group from PETN structure.

4. Conclusion

In summary, we explained the non-isothermal decomposition kinetics of PETN by studying both the products and reactants by a TGA-MS and DSC respectively. The activation energy for NO₂ showed similar values in the whole conversion range. Average activation energy of NO₂ production is ~175.8 kJ/mol. This is consistent with the theoretical value RO–NO₂ bond energy. Isoconversional kinetic analysis by the DSC observation in closed pan showed that activation energy of PETN decomposition is almost constant (~170 kJ/mol) across $\alpha=0.1-0.9$, and consistent with the activation energy of the generation of NO₂ from PETN decomposition. This indicates that dissociation NO₂ from PETN structure might be the rate limiting steps for the PETN decomposition. Activation energy of PETN, obtained from open pan DSC, are lower compared to the activation energy obtained from closed pan DSC and TGA-MS experiments. From this study, we conclude that activation energy for PETN decomposition is in the range of ~170–176 kJ/mol.

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303 Figure 1(a): Molecular structure of PETN
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Figure 2: NO₂ evolution from PETN decomposition observed in TGA-MS.

328 Figure 3: PETN single crystal in DSC at various heating rate in open and closed pan.

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Figure 4: Comparison of the extent of reaction of NO_2 generation observed in TGA-MS and overall PETN decomposition observed in DSC.

339 Figure 5: KAS plot, showing the decomposition kinetics, of gas evolution observed in TGA-MS
 340 and over all decomposition observed in DSC; here — for TGA-MS, — for DSC Open Pan
 341 and — for DSC Closed Pan.

Figure 6 : Comparison of activation energy of PETN obtained from gas evolution kinetics observed by a TGA-MS and heat released from the reaction observed in DSC.

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361 Figure 7: H₂O evolution from PETN decomposition observed in TGA-MS.

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