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Autocatalytic thermal decomposition kinetics of TNT

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Abstract

Thermal analysis has been employed to determine the kinetics and the energetics of the slow cook-off chemistry of 2,4,6-trinitrotoluene (TNT) by isothermal differential scanning calorimetry (DSC) in high-pressure crucibles sealed under air. Model-free isoconversional analysis of the DSC kinetic traces has been used to determine activation energies (E_α) and the functional form of the reaction model (dependence of reaction rate on the extent of conversion, α). While the variation in E_α with α is in qualitative agreement with the literature it is nevertheless constant within the 95% confidence limits at 140 ± 10 kJ mol^{-1}. Hence, no systematic variation in E_α occurs over the course of the reaction. Rather, the reaction model exhibits a large increase in the range $0.1 < \alpha < 0.25$ and a decrease for $0.25 < \alpha < 0.43$. Thus, the observed acceleratory period is caused by an increase in the reaction model, not by a decrease in activation energy, as might be expected for autocatalysis. This kinetic behavior is ascribed to nucleation and growth of reaction centers in liquid state TNT. In addition, a heat of reaction, $Q = (4.9 \pm 1.5) \times 10^2$ kJ mol^{-1} during the thermal decomposition of TNT has been shown to be independent of the heating rate and sample size. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2,4,6-Trinitrotoluene; Differential scanning calorimetry; Isoconversional

1. Introduction

Despite the vigorous search for new high explosives to replace 2,4,6-trinitrotoluene (TNT), it continues to find use because it can be meltcast with other materials including explosives, it is relatively inexpensive, it is relatively insensitive to impact and friction, and it is thermal stable [1]. The widespread and long-term use of TNT has led to extensive study of its thermal and explosive properties.

The determination of the kinetics and mechanism of the thermal decomposition of TNT remains a fundamental aspect of its characterization. Efforts on this scientific front have led to some seemingly contradictory findings, which often result from comparing results collected under different experimental conditions. Brill and James (BJ) have made considerable progress in reconciling the kinetics and mechanism of the thermal decomposition of TNT in reviews of TNT [2] and of nitroaromatic explosives [1]. By plotting the temperature of reaction versus the time to explosion (TTX), they determined that oxidation reactions of the –CH_3 moiety and C–NO_2 homolysis were isokinetic at a temperature of 770 °C and a time of 0.1 ms [1,2]. Oxidation reactions of the –CH_3 moiety dominate the initiation chemistry of TNT thermal decomposition below 770 °C and C–NO_2 homolysis dominates above 770 °C. At longer times ($t > 0.1$ s), catalysis by the decomposition products of TNT controls the TTX.

BJ have also compiled reported activation parameters for the thermal decomposition of TNT below

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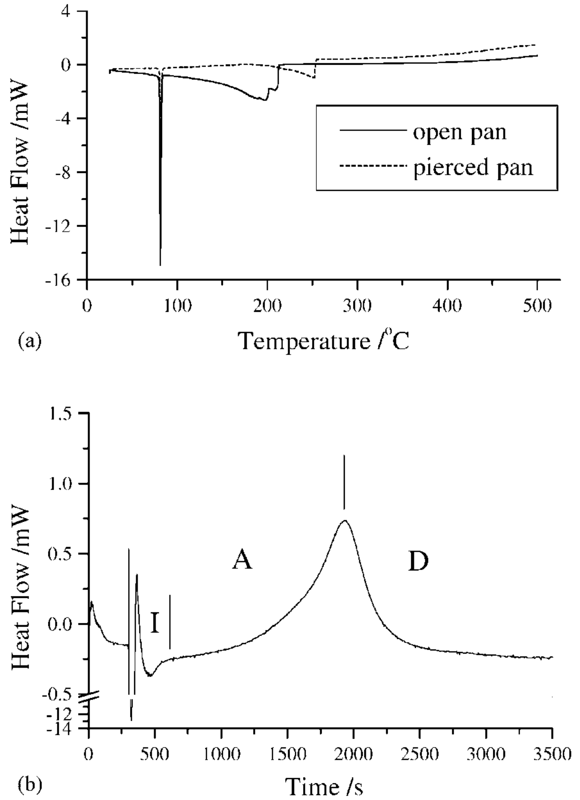

Fig. 1. (a) Open and pierced pan non-isothermal DSC curves of TNT each collected at a constant heating rate of $\beta = 10.0$ °C min^{-1}. (b) An isothermal DSC trace collected for a closed pan sample of TNT at a temperature of $T = 260$ °C showing the induction stage (I), the acceleratory stage (A), and the decay stage (D). The inclusion of an initial 5 min isothermal segment at $T = 150$ °C facilitated the data collection (see text).

500 °C [1,2]. Following the terminology used in two isothermal differential scanning calorimetry (DSC) studies [3,4], BJ assign three regions to the energy release trace of TNT: the induction phase, the acceleratory phase, and the decay phase (Fig. 1b). Activation energies between 171 and 212 kJ mol^{-1} have been assigned to –CH$_3$ oxidation in the induction phase and values between 126 and 149 kJ mol^{-1} have been attributed to catalysis by decomposition products in the acceleratory phase ([1] and references therein). An activation energy for the decay phase of 123 kJ mol^{-1} has also been reported [4]. Hence, the literature suggests that the activation energy changes during the thermal decomposition of TNT. The aforementioned studies in [1] have attempted to determine global activation parameters, and assign rate-limiting processes in some cases, for specific stages of the decomposition.

The present work provides the first description of the variation in the activation energy and the reaction model for the slow chemistry ($t \geqslant 0.1$ s) of TNT that is characteristic of cook-off below 500 °C. The high vapor pressure of TNT necessitated the use of sealed crucibles and DSC analysis to monitor its thermal decomposition. The application of model-free isoconversional analysis [5,6] to isothermal DSC traces in this study has shown that the reaction model, not the activation energy, is responsible for the increase in the rate of thermal decomposition during the autocatalytic period.

The activation energy and the reaction model have both been successfully described as a function of a continuous reaction progress variable, α, using isoconversional analysis. By detecting any variation in either of these two kinetic parameters, the autocatalysis that has been previously reported in the TNT literature has been described, herein, in a natural way. This study reports the first application of isoconversional analysis to the thermal decomposition of TNT. Isoconversional kinetic analysis has also been successfully applied to the thermal decomposition of several explosives including HMX, [7] RDX, [8] TNAZ, [9] and NTO. [10] Such analysis for TNT has provided a new description of the autocatalysis [7] that occurs during its thermal decomposition.

2. Experimental

2.1. Sample purification

TNT, was synthesized by the nitration of toluene according to the literature [11]. It was purified by recrystallization from ethanol, dried in air and had a melting point of 81 °C, which compares favorably with the literature value of 80.5 °C [12].

2.2. Differential scanning calorimetry

A Mettler-Toledo DSC821^{e} module was used to collect DSC curves with both isothermal and non-isothermal heating programs. In all DSC traces, positive going features correspond to exothermic processes and negative going features represent endothermic processes. The N_2 carrier gas flowed at a rate of 80 ml min^{-1}. 40 μL Al pans were used in open pan and pierced pan experiments. Samples sizes of ~1.0 mg in an open pan and ~0.5 mg in a pierced pan were used in experiments performed at a heating rate of $\beta = 10.0\ ^\circ\text{C min}^{-1}$ over a temperature range of 25–300 °C. In the pierced pan experiment, a 1.0 mm piercer was used to puncture pans lidded with crimp-sealed Al piercing lids. Closed pan DSC experiments employed 30 μL stainless steel crucibles (Mettler-Toledo) sealed under air. The crucibles are designed to contain up to 100 atm pressure, but the sample sizes were selected to be sufficiently small that the calculated final pressure inside the sealed crucibles did not exceed 15 atm. The integrated and normalized heat release was determined in non-isothermal experiments as a function of the heating rate and of the mass. The heating rate dependence used sample sizes of ~0.2 mg and was determined for $\beta = 2.5$, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, and 20.0 °C min^{-1} for a temperature range of 25–300 °C. The mass dependence was determined for a mass range of 75–425 μg at $\beta = 10.0\ ^\circ\text{C min}^{-1}$ for temperatures of 25–300 °C. The DSC instrument was calibrated for both temperature and heat flow using indium and aluminum melting point standards. Activation energies, Arrhenius pre-exponential factors and the numerically evaluated reaction models were determined from isoconversional analysis [9] of isothermal DSC kinetic traces collected at temperatures of 255, 260, 265, 270, and 275 °C. An initial 5 min isothermal segment at 150 °C, a temperature at which no thermal decomposition was observed to occur, preceded each isothermal experiment. This initial segment was used to avoid difficulties associated with instrument settling from a large temperature jump at the beginning of the experiment. For the isothermal DSC trace collected at 265 °C, typical of the other isothermal experiments, the temperature increased from 150 to 265 °C within 2 s with a 1.6 °C overshoot and stabilized to ±0.1 °C of the desired temperature within 90 s.

2.3. Error limits

Error limits shown in the E_α versus α plot and reported for the exothermic heat release Q are given as 95% confidence limits.

3. Kinetic analysis

3.1. Isoconversional analysis

A single step kinetic equation is frequently employed in the kinetic analysis of solid state reactions [13]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ae^{-E/RT}f(\alpha) \tag{1}$$

where α is the extent of reaction, $f(\alpha)$ is the reaction model, and the Arrhenius equation has been substituted for the temperature dependent rate constant, $k(T)$. Flynn and Wall [14] and Ozawa [15] first successfully applied integral methods to thermochemical data acquired at several constant heating rates to determine activation energies. Vyazovkin developed a more general isoconversional method that can be applied to an arbitrary temperature program [16]. For such conditions, Eq. (1) can be integrated to yield

$$\int_0^\alpha \frac{d\alpha}{\alpha} = f(\alpha) = A\int_0^{t_\alpha} e^{-E/RT(t)}\,dt = AJ[E, T(t_\alpha)] \tag{2}$$

where the subscript α represents the values pertaining to a given extent of conversion. From the fundamental assumption of isoconversional analysis that the reaction model is independent of the heating program [5], the right hand sides are equal for each temperature program. Hence, for n experiments carried out at different temperature programs, the activation energy, E_α, can be determined at any given α by minimizing the function

$$S^2(E_\alpha) = \frac{1}{n(n-1)}\sum_{i=1}^{n}\sum_{j\neq i}^{n}\left(\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} - 1\right)^2 \tag{3}$$

where the subscripts i and j depict ordinal numbers of two experiments conducted under different temperature programs. The J-integrals in Eq. (3) can be determined numerically using the trapezoid rule. The α-dependence of E_α is obtained by repeating the minimization procedure for each value of α. Any variation in the activation energy with α can be accounted for by breaking the kinetic traces into segments [6]. Then numerical integration of the $T(t)$ data over the segment determines the Arrhenius integral for each segment.

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t\alpha} e^{-E/RT(t)}\,dt \tag{4}$$

These integrals are used in Eq. (3) to determine the characteristic activation energy for each segment of the reaction. In Eq. (4), α varies from $\Delta\alpha$ to $1 - \Delta\alpha$ with an increment $\Delta\alpha = m^{-1}$, where m is the number of α values used in the analysis (typically 10–50).

3.2. Confidence intervals

Confidence intervals for E_α have been estimated on the basis of statistical criteria according to the method described earlier [5]. Ideally, the J-integrals (Eq. (4)) for any given segment $(t_{\alpha-\Delta\alpha} - t_\alpha)$ should be equal for every experiment from the fundamental assumption of the isoconversional kinetic method (c.f. Eq. (2)). The variance $S^2(E_\alpha)$ computed from Eq. (3) is a statistical measure of distribution of J-integral values that is independent of the number of experiments, n, in the limit where n becomes large. Minimization of the variance $S^2(E_\alpha)$ gives the optimum value of the activation energy $E_{\min}$. The error statistics constructed as

$$\Psi(E_\alpha) = \frac{S^2(E_\alpha)}{S^2_{\min}} \tag{5}$$

have the F-distribution [17]. These statistics allow the confidence limits for $E_{\min}$ to be determined by estimating the confidence limits for $S^2_{\min}$. The condition

$$\Psi(E_\alpha) < F_{1-p,n-1,n-1} \tag{6}$$

can be used to determine the 95% confidence interval for $S^2_{\min}$ by using $P = 0.95$ in Eq. (6). Here, $F_{1-p,n-1,n-1}$ is the percentile of the F-distribution for the $(1 - P) \times 100\%$ confidence probability. Then, the lower and upper confidence limits, E^{lo}_α and E^{up}_α, can be estimated for $E^{\min}_\alpha$ as the values of E_α for which $\Psi(E_\alpha) = F_{1-p,n-1,n-1}$.

4. Results

4.1. Open and pierced pan samples

Fig. 1a shows that open pan and pierced pan non-isothermal DSC traces both display a sharp endotherm at 81 °C that has been attributed to melting (vide infra). A broad endotherm occurs at higher temperatures over a range of 85–220 °C in open pan samples and over 180–255 °C in pierced pan samples. This behavior is consistent with the vaporization of TNT (vide infra).

4.2. Closed pan samples

To isolate and observe thermal decomposition, TNT samples were sealed in high-pressure crucibles. The integrated and normalized heat release of TNT samples under these conditions was determined by non-isothermal DSC. The heat release is largely independent of the heating rate and of the sample size and determined to be $Q = (4.9 \pm 1.5) \times 10^2$ kJ mol^{-1} (Fig. 2).

Isothermal DSC was employed to determine the Arrhenius parameters for thermal decomposition kinetics of TNT. Fig. 1b displays a typical isothermal DSC trace that results from subtraction of a blank curve for an empty pan experiment run using the same

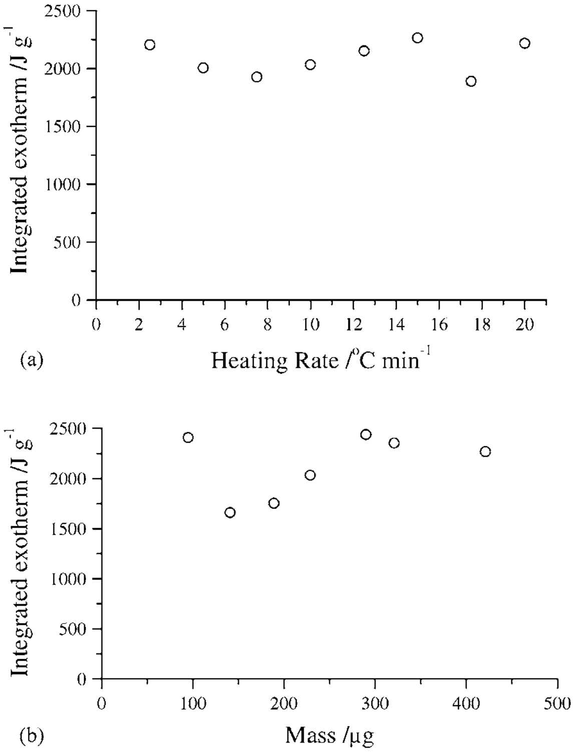

Fig. 2. (a) Plot of the integrated and normalized heat release in non-isothermal DSC traces as a function of heating rate for closed pan samples of TNT. (b) A plot of the integrated and normalized exotherm versus mass in non-isothermal DSC traces for closed pan samples of TNT heated at 10 °C min^{-1}.

temperature program. The sharp endotherm at a time of 300 s results from incomplete subtraction of the blank run and from the transition from a 150 °C isothermal segment to the desired isothermal temperature of 260 °C. For this temperature, a broad exotherm that covers the acceleratory and decay regions assigned in Fig. 1b occurs over a time of 700–3000 s. Applying isoconversional kinetic analysis to the exotherm reveals that E_α remains constant within the 95% confidence limits. The small variation that does occur includes an increase in E_α from 136 kJ mol^{-1} at $\alpha = 0.03$ to 169 kJ mol^{-1} at $\alpha = 0.27$ and decreases to 116 kJ mol^{-1} for $\alpha = 0.85-0.93$ (Fig. 3a). Similar analysis shows that the product of the pre-exponential factor and reaction model increases significantly from $Af(\alpha) = 3.3 \times 10^{10}\ \mathrm{s}^{-1}$ at $\alpha = 0.11$ to $9.3 \times 10^{13}\ \mathrm{s}^{-1}$ at $\alpha = 0.25$ prior to a sharp decrease to $1 \times 10^{12}\ \mathrm{s}^{-1}$ at $\alpha = 0.43$ (Fig. 3b).

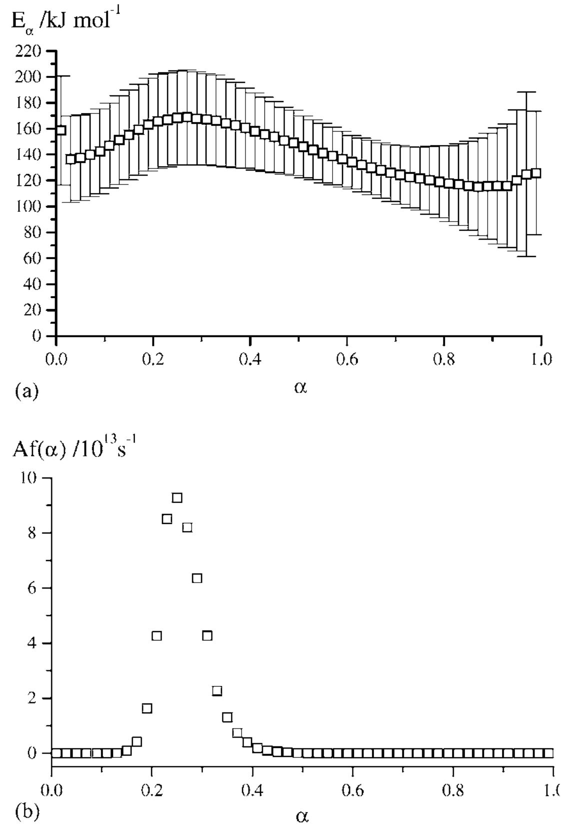

Fig. 3. (a) Activation energy (E_α) versus extent of reaction (α) plot obtained by isoconversional kinetic analysis of isothermal DSC traces of TNT such as in Fig. 1b for temperatures of $T = 255$, 260, 265, 270, 275 °C. The error bars indicate 95% confidence limits. (b) Product of pre-exponential factor and the reaction model, $Af(\alpha)$, versus α plot obtained using isoconversional analysis as in (a).

5. Discussion

5.1. Open and pierced pan samples

The sharp endotherm that occurs at 81 °C in non-isothermal DSC traces for both open and pierced pan samples has previously been assigned to melting [2] (Fig. 1a). The broader endotherm that occurs over a temperature range of 85–220 °C in open pan samples is indicative of vaporization [18]. The shift of the endotherm to higher temperatures in pierced pan samples results from the suppression of vaporization in a semi-confined system.

5.2. Closed pan samples: non-isothermal DSC traces

An integrated and normalized heat release of $Q = (4.9 \pm 1.5) \times 10^2$ kJ mol^{-1} (Fig. 2) for the thermal decomposition of TNT was determined in sealed crucibles designed to simulate cook-off conditions. Non-isothermal DSC was used to show that the heat release is independent of the heating rate and the sample size. A measured Q that is significantly smaller than reported enthalpies of combustion of $\Delta H_{\mathrm{combust}} = 3400$ kJ mol^{-1} [19] shows that the heat evolved in closed pan DSC experiments from nucleation and growth processes (vide infra) differs significantly from the heat released during combustion.

5.3. Closed pan samples: Isothermal DSC traces

The isothermal DSC trace of a closed pan TNT sample in Fig. 1b shows the characteristic induction, acceleratory, and decay regions. The application of isoconversional analysis to the exotherm yields activation energies and the reaction model as a function of α, [9] for the acceleratory and decay periods (Fig. 2a). The variation in the activation energy over the entire reaction is constant within the 95% confidence limits. Thus, while the E_α versus α profile is qualitatively consistent with literature values for the acceleratory and decay periods, ([1] and references therein) no systematic variation in the activation energy can be ascribed when considering the confidence intervals. The weighted average value of the activation energy over the course of the entire reaction is $E_\alpha = 140 \pm 10\ \text{kJ mol}^{-1}$.

In contrast to the nearly constant E_α, a sharp increase and decrease in the product $Af(\alpha)$, with α occurs during the acceleratory period over the interval, $\alpha = 0.11-0.43$. Thus, the enhancement in the rate of thermal decomposition during the acceleratory period is due to the reaction model, not to the activation energy. Since the temperature sensitivity of the reaction is expressed by E_α, the acceleratory behavior described by the reaction model should exist at all temperatures.

The isothermal experiments conducted over the temperature range of 255–275 °C have also been used to help identify the processes responsible for the rate enhancement during the acceleratory phase of TNT thermal decomposition. Using the Antoine equation to determine the equilibrium vapor pressure over this temperature range, [19] the fraction of TNT in the gas phase in a 30 μL sealed crucible, assuming no decomposition, ranges from 6.6 to 11%. Thus, ≥89% of the TNT sample in the crucible is in the liquid phase. For the acceleratory stage of the decomposition ($0.11 < \alpha < 0.25$) during which the reaction model shows a sharp increase from $Af(\alpha) = 3.3 \times 10^{10}$ to $9.3 \times 10^{13}\ \text{s}^{-1}$ (Fig. 3b), the activation energy is essentially constant (Fig. 3a). Such an increase in E_α most likely does not result from gas phase autocatalysis since the radicals or intermediates formed in such a process typically lead to a decrease in the activation energy [20]. Furthermore, the rate enhancement also cannot be due to a surface area effect as has been observed for solid β-HMX [7] because TNT has melted well prior to its observed thermal decomposition (vide supra). Rather, since TNT is mostly in the liquid state for the temperature range over which its thermal decomposition was observed to occur, it most likely undergoes liquid phase autocatalysis. The absence of a decrease in the activation energy during the rate acceleration is consistent with the nucleation and growth of reaction centers, [13] but their exact nature remains unknown. Such a determination exceeds the scope of the present study that was carried out to probe the decomposition kinetics and Arrhenius parameters that are characteristic of TNT cook-off chemistry, but provides fertile ground for future work.

6. Conclusions

The application of isoconversional kinetic analysis to isothermal DSC traces has determined the variation in the activation energy and the reaction model during the thermal decomposition of TNT for the first time. No systematic variation in the activation energy over the course of the reaction can be ascribed to thermal decomposition since the change in the E_α with α is within the 95% confidence limits. However, a large variation in the reaction model during the acceleratory period appears to result from nucleation and growth of reaction centers in the liquid portion of the confined TNT sample.

Acknowledgements

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