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# Estimation of the critical rate of temperature rise for thermal explosion of autocatalytic decomposing reaction of nitrocellulose using non-isothermal DSC

Binke Ning[a], Rongzu Hu[a,b,*], Hai Zhang[b,c], Zhiming Xia[b,c], Pengjiang Guo[b,c], Rong Liu[a], Guie Lu[d], Jinyong Jiang[d]

[a] *Xi'an Modern Chemistry Research Institute, Xi'an 710065, China*
[b] *Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an 710069, China*
[c] *Department of Mathematics, Northwest University, Xi'an 710069, China*
[d] *Ordnance Engineering Institute, Shijiazhuang 05000, China*

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## Abstract

A method of estimating the critical rate of temperature rise for thermal explosion of empiric-order autocatalytic decomposition reaction system using non-isothermal DSC is presented. Information is obtained on the increasing rate of temperature in nitrocellulose containing 12.97% of nitrogen when the first-order autocatalytic decomposition converts into thermal explosion.

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## 1. Introduction

The critical temperature ($T_b$) and critical rate of temperature rise $(\mathrm{d}T/\mathrm{d}t)_{T_b}$ for thermal explosion of the autocatalytic decomposition reaction systems are two important parameters from the point of views of the evaluation of safety and transition from thermal decomposition to thermal explosion for energetic materials (EMs). In the field of estimating these parameters, two methods for estimating the value of $T_b$ of an autocatalytic overall reaction system and a method for estimating the value of $(\mathrm{d}T/\mathrm{d}t)_{T_b}$ of first-order autocatalytic reaction system, using non-isothermal DSC have been reported [1–7], but no method for estimating the value of $(\mathrm{d}T/\mathrm{d}t)_{T_b}$ of empiric-order autocatalytic reaction system. In this work, we studied a method of estimating the value of $(\mathrm{d}T/\mathrm{d}t)_{T_b}$ of empiric-order autocatalytic reaction system. For easy comparison, the notation and procedures used to derive the estimation formula of $T_b \sim (\mathrm{d}T/\mathrm{d}t)_{T_b}$ relation in this work are the same as those of Hu et al. [1,2,6] and Zhang et al. [7].

## 2. Theoretical and method

The enthalpy ($q_1$) of thermal decomposition reaction per unit time for EMs can be expressed by the equation:

$$q_1 = \frac{QVd}{M}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \quad (1)$$

where $Q$ is the enthalpy of the thermal decomposition reaction in $\mathrm{J\,mol^{-1}}$, $V$ the volume of EMs loaded in $\mathrm{cm^3}$, $d$ the loading density in $\mathrm{g\,cm^{-3}}$, $M$ the mole mass of EMs in $\mathrm{g\,mol^{-1}}$ and $\mathrm{d}\alpha/\mathrm{d}t$ the reaction rate.

The thermal decomposition, as an autocatalytic reaction, can be described by the following equations:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \quad (2)$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} 2\mathrm{B} \quad (3)$$

where A represents the initial reactant and B the thermal decomposition product. The rate expression that corresponds to this scheme is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_1(1-\alpha)^m + k_2\alpha^n(1-\alpha)^p \quad (4)$$

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[*] Corresponding author.
*E-mail address:* hurongzu@public.xa.sn.cn (R. Hu).

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where $\alpha$ stands for the conversion degree, for DSC curve, $\alpha = H_t/H_0$, where $H_0$ is the total exothermicity of the MEs (corresponding to the global area under the DSC curve) and $H_t$ is the reaction heat in a certain time (corresponding to the partial area under the DSC curve); $k_1 = A_1 \exp(-E_{a1}/RT)$, $k_2 = A_2 \exp(-E_{a2}/RT)$, where $A_1$ and $A_2$ are the pre-exponential factors, $E_{a1}$ and $E_{a2}$ the activation energies for the autocatalytic reaction, $T$ the temperature and $t$ the time; $m$, $n$ and $p$ the apparent reaction orders. For the first-order autocatalytic decomposition reaction, $m = n = p = 1$.

Substituting Eq. (4) into Eq. (1) gives

$$q_1 = \frac{QVd}{M}\left[A_1 \exp\left(-\frac{E_{a1}}{RT}\right)(1-\alpha)^m + A_2 \exp\left(\frac{-E_{a2}}{RT}\right)\alpha^n (1-\alpha)^p\right] \tag{5}$$

where $\alpha_b$ is the value of $\alpha$ corresponding to $T_b$, $k_{1b} = A_l \exp(-E_{a1}/RT_b)$, $k_{2b} = A_2 \exp(-E_{a2}/RT_b)$, where $T_b$ is the critical temperature of thermal explosion of EMs in $K$ and Eq. (6) becomes

$$q_2|_{T_b} = k'(T_b - T_{e0})S \tag{8}$$

where $T_{e0}$ is the onset temperature in the DSC curve under linear temperature increase condition when $\beta$ tends to zero.

According to the $q_1$–$T$ and $q_2$–$T$ relations, the sufficient and essential conditions from thermal decomposition to thermal explosion can be expressed as

$$q_1|_{T_b} = q_2|_{T_b} \tag{9}$$

$$\left.\frac{dq_1}{dT}\right|_{T_b} = \left.\frac{dq_2}{dT}\right|_{T_b} \tag{10}$$

Differentiation of Eq. (5) with respect to $t$ gives
t

$$\left.\frac{dq_1}{dT}\right|_{T=T_b,\alpha=\alpha_b} = QVd\frac{[((dT/dt)_{T_b}/RT_b^2)(k_{1b}E_{a1}(1-\alpha_b)^m + k_{2b}E_{a2}\alpha_b^n(1-\alpha_b)^p) + (k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)[k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - k_{1b}m(1-\alpha_b)^{m-1}]]}{M(dT/dt)_{T_b}} \tag{11}$$

At the same time, the amount of heat ($q_1$) transferred by the wall of the reactor to surrounding medium in unit time is

$$q_2 = k'(T - T_c)S \tag{6}$$

where $k'$ is an overall heat transfer coefficient in J cm$^{-2}$ K$^{-1}$ s$^{-1}$; $T_c$ the temperature of the reaction wall and surroundings according to the linear relationship $T_c = T_0 + \beta t$, where $\beta$ is the heating rate in K min$^{-1}$, $T_0$ the initial temperature at which the DSC curve deviates from the baseline in K; $S$ the external surface of the loaded sample in cm$^2$.

With the boundary conditions of thermal explosion, Eq. (5) becomes

$$q_1|_{T_b} = \frac{QVd}{M}[k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p] \tag{7}$$

where $(dT/dt)_{T_b}$ is the increasing rate of temperature in EMs when thermal decomposition converts into thermal explosion. This is difficult to solve directly from conventional experiments.

Differentiation of Eq. (6) with respect to $t$ gives

$$\left.\frac{dq_2}{dT}\right|_{T=T_b} = \frac{k'S}{(dT/dt)_{T_b}}\left[\left(\frac{dT}{dt}\right)_{T_b} - \beta\right] \tag{12}$$

Combining Eqs. (7)–(9), yields

$$\frac{QVd}{M}\left[k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p\right] = k'S(T_b - T_{e0}) \tag{13}$$

Combining Eqs. (10)–(12), yields

$$QVd\frac{[((dT/dt)_{T_b}/RT_b^2)(k_{1b}E_{a1}(1-\alpha_b)^m + k_{2b}E_{a2}\alpha_b^n(1-\alpha_b)^p) + (k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)[k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - k_{1b}m(1-\alpha_b)^{m-1}]]}{M(dT/dt)_{T_b}} = \frac{k'S}{(dT/dt)_{T_b}}\left[\left(\frac{dT}{dt}\right)_{T_b} - \beta\right] \tag{14}$$

As the thermal explosion starts, $(dT/dt)_{T_b} \gg \beta$ and Eq. (14) may be simplified to the following form:

$$QVd\frac{[((dT/dt)_{T_b}/RT_b^2)(k_{1b}E_{a1}(1-\alpha_b)^m + k_{2b}E_{a2}\alpha_b^n(1-\alpha_b)^p) + (k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)[k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - k_{1b}m(1-\alpha_b)^{m-1}]]}{M(dT/dt)_{T_b}} = k'S \tag{15}$$

Combining Eqs. (13) and (15), we get

$$\left(\frac{dT}{dt}\right)_{T_b} = \frac{(T_b - T_{e0})(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)(k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - k_{1b}m(1-\alpha_b)^{m-1})}{(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p) - (T_b - T_{e0})(k_{1b}(E_{a1}/RT_b^2)(1-\alpha_b)^m + k_{2b}(E_{a2}/RT_b^2)\alpha_b^n(1-\alpha_b)^p)} \tag{16}$$

Eq. (16) is the relation formula for estimating the critical rate of temperature rise in EMs when the apparent empiric-order autocatalytic decomposition converts into thermal explosion.

Once the values of $E_{a1}$, $E_{a2}$, $A_1$, $A_2$, $T_{e0}$, $T_b$, $\alpha_b$, $m$, $n$ and $p$ have been calculated from an analysis of the DSC curves under the same experimental conditions, the corresponding value of $(dT/dt)_{T_b}$ can then be obtained from Eq. (16).

## 3. Experimental

### 3.1. Materials

Nitrocellulose containing 12.97% of nitrogen (NC (12.97% N)) used in this work was prepared and purified at Xi'an Modern Chemistry Research Institute.

### 3.2. Instrument and conditions

In the present experiments, the initial data needed for calculating all the kinetic parameters were obtained using a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminium cell. The conditions of the DSC analyses were: sample mass, about 0.7 mg; heating rates, 1, 2, 5, 10, 18 and 20 $\mathrm{K\,min^{-1}}$; calorimetric sensitivities, ±20.92 and 41.84 $\mathrm{mJ\,s^{-1}}$; atmosphere, static air; reference sample, $\alpha$-$Al_2O_3$; the precision of temperature was 0.25 K; the temperature and heat were calibrated using pure indium and tin powders. Heating rate $\beta$ was calculated according to the actual rising rate of temperature from 50 °C to the temperature at the end of reaction.

## 4. Results and discussion

The original data ($T_i$, $\alpha_i$, $i = 1, 2, \ldots, 22$) taken from the DSC curve at a heating rate of 18 $\mathrm{K\,min^{-1}}$ are shown in Table 1. The measured values of $\beta_i$ and $T_{ei}$ ($i = 1, 2, \ldots, 5$), the calculated value of $E_{ke}$ by the Kissinger's method [8], the values ($T_{e0}$) of $T_e$ corresponding to $\beta \to 0$ obtained by Eq. (17) taken from [3], the values of $T_b$ obtained by Eq. (18) taken from [3], and the value of $\alpha_b$ corresponding to $T_b$ obtained by the data in Table 1 are shown in Table 2:

$$T_{ei} = T_{e0} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1, 2, \ldots, 5 \tag{17}$$

$$T_b = \frac{E_{ke} - \sqrt{E_{ke}^2 - 4E_{ke}RT_{e0}}}{2R} \tag{18}$$

The calculated values of $E_{a1}$, $E_{a2}$, $A_1$ and $A_2$ by the reported method in the literatures [5,9–11] are given in Table 3. By substituting the values of $T_{e0}$, $T_b$ and $\alpha_b$ in Table 2, and $E_{a1}$, $E_{a2}$, $A_1$ and $A_2$ in Table 3, and $m = n = p = 1$ (because the thermal decomposition of NC is a typical first-order autocatalytic reaction) into Eq. (16), the value of $(dT/dt)_{T_b}$ listed in Table 3 is obtained.

Table 1
Thermal decomposition data of NC (12.97% N) determined by DSC

| No. | $T_i$ (K) | $\alpha_i$ |
|---|---|---|
| 1 | 355.49 | 0.0305 |
| 2 | 360.23 | 0.0313 |
| 3 | 364.69 | 0.0315 |
| 4 | 369.04 | 0.0321 |
| 5 | 373.62 | 0.0323 |
| 6 | 378.47 | 0.0327 |
| 7 | 383.55 | 0.0335 |
| 8 | 388.86 | 0.0343 |
| 9 | 409.68 | 0.0346 |
| 10 | 414.69 | 0.0352 |
| 11 | 419.61 | 0.0364 |
| 12 | 424.60 | 0.0394 |
| 13 | 429.60 | 0.0401 |
| 14 | 434.65 | 0.0415 |
| 15 | 439.70 | 0.0433 |
| 16 | 449.76 | 0.0449 |
| 17 | 454.79 | 0.0503 |
| 18 | 459.86 | 0.0586 |
| 19 | 464.92 | 0.0721 |
| 20 | 470.04 | 0.0986 |
| 21 | 475.38 | 0.1618 |
| 22 | 481.19 | 0.3128 |

Table 2
The calculated values of the critical temperature ($T_b$) of thermal explosion for NC (12.97% N)[a]

| Measured values | | Calculated values | | | |
|---|---|---|---|---|---|
| $\beta$ ($\mathrm{K\,min^{-1}}$) | $T_e$ (K) | $E_{ke}$ ($\mathrm{kJ\,mol^{-1}}$) | $T_{e0}$ (K) | $T_b$ (K) (Eq. (18)) | $\alpha_b$ |
| 1.031 | 451.95 | 176.7 | 446.45 | 456.24 | 0.055 |
| 2.146 | 458.90 | | | | |
| 5.131 | 465.45 | | | | |
| 10.59 | 472.65 | | | | |
| 21.59 | 481.45 | | | | |

[a] $\beta$, heating rate; $T_e$, onset temperature in the DSC curve; $E_{ke}$, apparent activation energy obtained by Kissinger's method; $T_{e0}$, the value of $T_e$ corresponding to $\beta \to 0$; $\alpha_b$, the value of $\alpha$ corresponding to $T_b$.

The results in Tables 2 and 3 show that: (1) Under our non-isothermal DSC conditions, the thermal decomposition of NC (12.97% N) can be described by the first-order autocatalytic equation:

$$\frac{d\alpha}{dt} = 10^{16.4} \exp\left(-\frac{210{,}380}{RT}\right)(1-\alpha) + 10^{16.7} \exp\left(-\frac{172{,}290}{RT}\right)\alpha(1-\alpha) \tag{19}$$

Table 3
Results for analyzing the data in Tables 1 and 2 by Eqs. (4) and (16)

| | |
|---|---|
| $E_{a1}$ ($\mathrm{kJ\,mol^{-1}}$) | 210.38 |
| $E_{a2}$ ($\mathrm{kJ\,mol^{-1}}$) | 172.29 |
| $A_1$ ($\mathrm{s^{-1}}$) | $10^{16.4}$ |
| $A_2$ ($\mathrm{s^{-1}}$) | $10^{16.7}$ |
| $(dT/dt)_{T_b}$ ($\mathrm{K\,s^{-1}}$) | 0.3247 |

(2) The value of the critical rate of temperature rise in NC (12.97 N%) when the decomposition reaction converts into thermal explosion is 0.3247 $\mathrm{K\,s^{-1}}$. (3) Because $(\mathrm{d}T/\mathrm{d}t)_{\mathrm{T_b}} \gg \beta$, we conclude that in the derivation process of Eq. (16), the assumption of adopting $((\mathrm{d}T/\mathrm{d}t)_{T_\mathrm{b}} - \beta)/(\mathrm{d}T/\mathrm{d}t)_{T_\mathrm{b}} = 1$ is rational.

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