

ESTIMATION OF THE CRITICAL RATE OF TEMPERATURE INCREASE OF THERMAL EXPLOSION OF NITROCELLULOSE USING NON-ISOTHERMAL DSC

Rong-zu Hu^{a*}, Peng-jiang Guo^{a, b}, Sheng-li Gao^a, Hai Zhang^{a, b}
Zhi-ming Xia^{a, b}, Bin-ke Ning^c, Yan Fang^a, Qi-zhen Shi^a and Rong Liu^d

^a Shaanxi Key Laboratory of Physico-Inorganic Chemistry and Department of Chemistry, Northwest University,
Xi'an 710069, China

^b Department of Mathematics, Northwest University, Xi'an 710069, China

^c Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

^d Department of Food Engineering, Nanchang University, Nanchang 330047, China

Abstract A method of estimating the critical rate of temperature increase of thermal explosion for the first order autocatalytic decomposition reaction system using non-isothermal DSC is presented. Information is obtained on the increasing rate of temperature in nitrocellulose containing 13.54% of nitrogen when the first order autocatalytic decomposition converts into thermal explosion.

Keywords DSC, Nitrocellulose, Increasing rate of temperature, Non-isothermal

INTRODUCTION

The critical temperature (T_b) and critical rate of temperature increase $\left(\frac{dT}{dt}\right)_{T_b}$ of thermal explosion for the first order autocatalytic decomposition reaction system are two important parameters from the point of view 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 using non-isothermal DSC have been reported^[1–6], but not for the value of $\left(\frac{dT}{dt}\right)_{T_b}$.

In this work, we develop a method of estimating the value of $\left(\frac{dT}{dt}\right)_{T_b}$. For easy comparison, the notation and procedures used to derive the estimation formula of the T_b - $\left(\frac{dT}{dt}\right)_{T_b}$ relation in this work are the same as those reported in the literature^[1–3, 6].

THEORY AND METHOD

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

* Corresponding author: Rong-zu Hu (胡荣祖), E-mail: hurongzu@public.xa.sn.cn

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

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

The thermal decomposition, as an autocatalytic reaction, can be described by Eqs. (2) and (3):



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

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) + k_2\alpha(1 - \alpha) \quad (4)$$

where α stands for the conversion degree. For the DSC curve, $\alpha = \frac{\int_{T_0}^T \left(\frac{dH}{dt} \right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH}{dt} \right) dT} = H_t/H_o$, where dH/dt is the

exothermic rate, T denotes the temperature at a certain time in the DSC curve, T_0 and T_∞ are the initial and final temperatures in the DSC curve, respectively; H_o is the total exothermicity of the MEs (corresponding to the global area under the DSC curve) and H_t is the reaction heat at 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, and E_{a1} and E_{a2} are the activation energies for the first-order and autocatalytic reaction, respectively; T stands for the temperature, t for the time.

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

$$q_1 = \frac{QVd}{M} (1 - \alpha) [A_1 \exp(-E_{a1}/RT) + A_2 \alpha \exp(-E_{a2}/RT)] \quad (5)$$

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

$$q_2 = k'(T - T_c)S \quad (6)$$

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

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

$$q_1|_{T_b} = \frac{QVd}{M} (1 - \alpha_b)(k_{1b} + k_{2b}\alpha_b) \quad (7)$$

where α_b is the value of α corresponding to T_b , $k_{1b} = A_1 \exp(-E_{a1}/RT_b)$, $k_{2b} = A_2 \exp(-E_{a2}/RT_b)$, where T_b is the critical temperature of thermal explosion of EMs in K, and Eq. (6) becomes

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

where T_{eo} is the onset temperature in the DSC curve under linear temperature increase condition when β 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

$$\left\{ q_1 \right|_{T_b} = q_2 \right|_{T_b} \quad (9)$$

$$\left\{ \frac{dq_1}{dT} \right|_{T_b} = \frac{dq_2}{dT} \right|_{T_b} \quad (10)$$

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

$$\frac{dq_1}{dT} \Big|_{T=T_b, \alpha=\alpha_b} = \frac{QVd(1-\alpha_b)}{M(dT/dt)_{T_b}} \left[-k_{1b}^2 + k_{2b}^2\alpha_b(1-2\alpha_b) + k_{1b}k_{2b}(1-3\alpha_b) + \frac{(dT/dt)_{T_b}}{RT_b^2} (k_{1b}E_{a1} + k_{2b}\alpha_bE_{a2}) \right] \quad (11)$$

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

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

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

Combining Eqs. (7), (8) and (9), yields

$$\frac{QVd}{M} (1-\alpha_b)(k_{1b} + k_{2b}\alpha_b) = k'S(T_b - T_{eo}) \quad (13)$$

Combining Eqs. (10), (11) and (12), yields

$$\begin{aligned} & \frac{QVd(1-\alpha_b)}{M(dT/dt)_{T_b}} \left[-k_{1b}^2 + k_{2b}^2\alpha_b(1-2\alpha_b) + k_{1b}k_{2b}(1-3\alpha_b) + \frac{(dT/dt)_{T_b}}{RT_b^2} (k_{1b}E_{a1} + k_{2b}\alpha_bE_{a2}) \right] \\ &= \frac{k'S}{(dT/dt)_{T_b}} \left[\left(\frac{dT}{dt} \right)_{T_b} - \beta \right] \end{aligned} \quad (14)$$

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

$$\frac{QVd(1-\alpha_b)}{M(dT/dt)_{T_b}} \left[-k_{1b}^2 + k_{2b}^2\alpha_b(1-2\alpha_b) + k_{1b}k_{2b}(1-3\alpha_b) + \frac{(dT/dt)_{T_b}}{RT_b^2} (k_{1b}E_{a1} + k_{2b}\alpha_bE_{a2}) \right] = k'S \quad (15)$$

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

$$\left(\frac{dT}{dt} \right)_{T_b} = \frac{RT_b^2(T_b - T_{eo})[-k_{1b}^2 + \alpha_b(1-2\alpha_b)k_{2b}^2 + k_{1b}k_{2b}(1-3\alpha_b)]}{RT_b^2(k_{1b} + \alpha_bk_{2b}) - (T_b - T_{eo})(E_{a1}k_{1b} + \alpha_bE_{a2}k_{2b})} \quad (16)$$

Equation (16) is the relation formula for estimating the rate of temperature increase in EMs when the first order autocatalytic decomposition converts into thermal explosion.

Once the values of E_{a1} , E_{a2} , A_1 , A_2 , T_{eo} , T_b and α_b 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).

EXPERIMENTAL

Materials

Nitrocellulose containing 13.54% of nitrogen [NC(13.54% N)] used in this work was prepared and purified at Xi'an Modern Chemistry Research Institute.

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 K min⁻¹, respectively; calorimetric sensitivities, ± 20.92 and 41.84 mJ s⁻¹; atmosphere, static air; reference sample, α -Al₂O₃; the precision of temperature was 0.25 K; the temperature and heat were calibrated using pure indium and tin powders. Heating rate β was calculated according to the actual rising rate of temperature from 50°C to the temperature at the end of reaction. DSC curves obtained under the same conditions overlap with each other, indicating that the reproducibility of tests is satisfactory.

RESULTS AND DISCUSSION

The original data (T_i , α_i , $i = 1, 2, \dots, 18$) taken from the DSC curve at a heating rate of 18 K min⁻¹ are shown in Table 1. The measured values of β_i and T_{ei} ($i = 1, 2, \dots, 5$), the calculated value of E_{ke} by Kissinger's method^[7], the values (T_{eo}) of T_e corresponding to $\beta \rightarrow 0$ obtained by the Eq. (17) taken from Ref. [3], the values of T_b obtained by the Eq. (18) taken from [3], and the value of α_b corresponding to T_b are shown in Table 2.

$$T_{ei} = T_{eo} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1, 2, \dots, 5 \quad (17)$$

$$T_b = \frac{E_{ke} - \sqrt{E_{ke}^2 - 4E_{ke}RT_{eo}}}{2R} \quad (18)$$

Table 1. Thermal decomposition data of NC (13.54%N) determined by DSC

No.	T_i (K)	α_i	No.	T_i (K)	α_i	No.	T_i (K)	α_i	No.	T_i (K)	α_i
1	385.32	0.0028	6	415.42	0.0049	11	445.51	0.0107	16	470.81	0.0749
2	390.49	0.0029	7	425.36	0.0054	12	450.55	0.0146	17	476.21	0.1518
3	400.63	0.0033	8	430.38	0.0063	13	455.55	0.0201	18	482.25	0.3388
4	405.58	0.0038	9	435.44	0.0075	14	460.60	0.0287			
5	410.48	0.0048	10	440.50	0.0082	15	465.66	0.0441			

Table 2. The calculated values of the critical temperature (T_b) of thermal explosion for NC (13.54% N)

Measured values		Calculated values			
β (K min ⁻¹)	T_e (K)	E_{ke} (kJ mol ⁻¹)	T_{eo} (K)	Eq.(18)	
				T_b (K)	α_b
1.015	451.95	180.2	441.74	451.13	0.016
2.044	458.90				
5.182	465.45				
11.68	472.65				
18.02	480.95				

β : heating rate; T_e : onset temperature in the DSC curve; E_{ke} : apparent activation energy obtained by Kissinger's method; T_{eo} : the value of T_e corresponding to $\beta \rightarrow 0$; α_b : the value of α corresponding to T_b

The values of E_{a1} , E_{a2} , A_1 and A_2 calculated by the reported method in literature^[5, 8–10] are given in Table 3. By substituting the values of T_{eo} , T_b and α_b in Table 2, and E_{a1} , E_{a2} , A_1 and A_2 in Table 3 into Eq. (16), the value of $(dT/dt)_{T_b}$ listed in Table 3 is obtained.

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

E_{a1} (kJ mol ⁻¹)	E_{a2} (kJ mol ⁻¹)	A_1 (s ⁻¹)	A_2 (s ⁻¹)	$(dT/dt)_{T_b}$ (Ks ⁻¹)
210.38	172.69	$10^{16.4}$	$10^{16.7}$	0.1112

The results in Tables 2 and 3 show that: (1) under our non-isothermal DSC conditions, the thermal decomposition of NC (13.54% N) can be described by the first order autocatalytic Eq. (19)

$$\frac{d\alpha}{dt} = 10^{16.4} \exp\left(-\frac{210380}{RT}\right)(1-\alpha) + 10^{16.7} \exp\left(-\frac{172690}{RT}\right)\alpha(1-\alpha)$$

(19)

(2) the value of the rate of temperature increase in NC (13.54%N) when the decomposition reaction converts into thermal explosion is 0.1112 K s⁻¹; (3) because $(dT/dt)_{T_b} \gg \beta$, we conclude that in the derivation process of Eq.

(18), the assumption of adopting $\frac{(dT/dt)_{T_b} - \beta}{(dT/dt)_{T_b}} = 1$ is rational.

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