Estimation of the critical rate of temperature rise for thermal explosion of first-order autocatalytic decomposition reaction systems using non-isothermal DSC

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Abstract

A method of estimating the critical rate of temperature rise for thermal explosion of first-order autocatalytic decomposition reaction systems using non-isothermal DSC is presented. Information is obtained on the increasing rate of temperature in highly nitrated nitrocellulose containing 14.14% of nitrogen when the first-order autocatalytic decomposition converts into thermal explosion. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The critical temperature (T_b) and the critical rate of temperature rise $(dT/dt)_{T_b}$ for thermal explosion of first-order 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 regard to 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 no method for

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estimating the value of $(\mathrm{d}T/\mathrm{d}t)_{T_b}$. In this work, we studied a method of estimating the value of $(\mathrm{d}T/\mathrm{d}t)_{T_b}$. 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 Rongzu et al. [1,2,6] and Tonglai et al. [3].

2. Theoretical

2.1. Basic theory of decomposition reaction

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

$$q_1 = \frac{QVd}{M}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{1}$$

where Q is the enthalpy of the thermal decomposition reaction in $\mathrm{J\,mol}^{-1}$, V the volume of EMs loaded in 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:

$$\mathrm{A} \overset{k_1}{\rightarrow} \mathrm{B} \tag{2}$$

$$\mathrm{A} + \mathrm{B} \overset{k_2}{\rightarrow} 2\mathrm{B} \tag{3}$$

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

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_1(1-\alpha) + k_2\alpha(1-\alpha) \tag{4}$$

where α stands for the conversion degree, for DSC curve, $\alpha = H_t/H_0$, where H_0 is the total exothermicity of the EMs (corresponding to the global area under the DSC curve) and H_t 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, and E_{a1} and E_{a2} are the activation energies for the first-order autocatalytic reaction, respectively; T is the temperature, t the time.

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

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

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 $\mathrm{J\,cm}^{-2}\,\mathrm{K}^{-1}\,\mathrm{s}^{-1}$, T_c 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 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.

2.2. Transition from decomposition to thermal explosion

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

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

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

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

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

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

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

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

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

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

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

Combining Eqs. (10)–(12), yields

$$\frac{QVd(1-\alpha_b)}{M(\mathrm{d}T/\mathrm{d}t)_{T_b}}\left[-k_{1b}^2 + k_{2b}^2\alpha_b(1-2\alpha_b) + k_{1b}k_{2b}(1-3\alpha_b)\right.$$
$$\left. + \frac{(\mathrm{d}T/\mathrm{d}t)_{T_b}}{RT_b^2}(k_{1b}E_{a1} + k_{2b}\alpha_b E_{a2})\right] = \frac{k'S}{(\mathrm{d}T/\mathrm{d}t)_{T_b}}\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{T_b} - \beta\right] \tag{14}$$

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

$$\frac{QVd(1-\alpha_b)}{M(\mathrm{d}T/\mathrm{d}t)_{T_b}}\left[-k_{1b}^2 + k_{2b}^2\alpha_b(1-2\alpha_b) + k_{1b}k_{2b}(1-3\alpha_b)\right.$$
$$\left. + \frac{(\mathrm{d}T/\mathrm{d}t)_{T_b}}{RT_b^2}(k_{1b}E_{a1} + k_{2b}\alpha_b E_{a2})\right] = k'S \tag{15}$$

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

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{T_b} = \frac{RT_b^2(T_b - T_{eo})[-k_{1b}^2 + \alpha_b(1-2\alpha_b)k_{2b}^2 + k_{1b}k_{2b}(1-3\alpha_b)]}{RT_b^2(k_{1b} + \alpha_b k_{2b}) - (T_b - T_{eo})(E_{a1}k_{1b} + \alpha_b E_{a2}k_{2b})} \tag{16}$$

the above equation is the relation formula for estimating the critical rate of temperature rise 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 $(\mathrm{d}T/\mathrm{d}t)_{T_b}$ can then be obtained from Eq. (16).

3. Experimental

3.1. Materials

Highly nitrated nitrocellulose containing 14.14% of nitrogen [HNNC (14.14% 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 aluminum 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, $\pm$20.92 and 41.84 mJ s^{-1}; atmosphere, static air; reference sample, α-Al$_2$O$_3$; 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.

4. Results and discussion

The original data ($T_i, \alpha_i, i = 1, 2, \ldots, 28$) 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} ($i = 1, 2, \ldots, 5$), the calculated value of E_{ke} by the Kissinger's method [7], the values (T_{eo}) 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 α_b corresponding to T_b are shown in Table 2:

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

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

The calculated values of E_{a1}, E_{a2}, A_1 and A_2 by the reported method in the 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 are obtained.

Table 1
Thermal decomposition data of HNNC (14.14% N) determined by DSC

Number	T_i (K)	α_i
1	367.87	0.033
2	371.99	0.034
3	376.19	0.035
4	380.37	0.036
5	384.64	0.037
6	388.99	0.038
7	393.34	0.039
8	397.76	0.040
9	402.26	0.042
10	406.72	0.043
11	411.24	0.044
12	415.78	0.045
13	420.28	0.047
14	424.80	0.048
15	429.32	0.049
16	433.82	0.051
17	438.33	0.052
18	442.80	0.054
19	447.27	0.056
20	451.75	0.059
21	456.22	0.062
22	460.71	0.067
23	465.20	0.075
24	469.73	0.088
25	474.33	0.110
26	479.03	0.156
27	484.06	0.262
28	489.61	0.492

Table 2
The calculated values of the critical temperature (T_b) of thermal explosion for HNNC (14.14% N)[a]

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
1.059	451.20	171.4	446.30	456.40	0.063
2.211	457.90				
5.202	465.70				
10.78	473.40				
21.39	481.70				

[a] 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 $\beta \to 0$; α_b: the value of α corresponding to T_b.

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})	$(\mathrm{d}T/\mathrm{d}t)_{T_b}$ (K min^{-1})
212.3	170.0	$10^{16.6}$	$10^{17.7}$	1083.6

The results in Tables 2 and 3 show that:

(1) Under our non-isothermal DSC conditions, the thermal decomposition of HNNC (14.14% N) can be described by the first-order autocatalytic equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 10^{16.6} \exp\left(-\frac{212300}{RT}\right)(1-\alpha) + 10^{17.7}\exp\left(-\frac{170000}{RT}\right)\alpha(1-\alpha) \quad (19)$$

(2) The value of the critical rate of temperature rise in HNNC (14.14% N) when the decomposition reaction converts into thermal explosion is 1083.6 K min^{-1}.

(3) Because $(\mathrm{d}T/\mathrm{d}t)_{T_b} \gg \beta$, we conclude that the derivation of Eq. (18), assuming $[(\mathrm{d}T/\mathrm{d}t)_{T_b} - \beta]/(\mathrm{d}T/\mathrm{d}t)_{T_b} = 1$, is rational.

References

[1] H. Rongzu, Y. Zengquan, L. Yanjun, W. Shanxiang, Baozha Yu Chongji 7 (4) (1987) 348–351.
[2] X. Yi, H. Rongzu, Y. Chaoqing, F. Guofu, Z. Jihua, Propellants Explosives Pyrotech. 17 (6) (1992) 298–302.
[3] Z. Tonglai, H. Rongzu, X. Yi, L. Fuping, Thermochim. Acta 244 (3) (1994) 171–176.
[4] S. Qizhen, Y. Haike, Z. Fengqi, H. Rongzu, Thermoanalysis Kinetics and Thermokinetics, Shaanxi Scientific and Technical Press, Xi'an, China, 2001, p. 194.
[5] H. Rongzu, S. Qizhen, Thermal Analysis Kinetics, Science Press, Beijing, China, 2001, p. 175.
[6] L. Rong, N. Binke, W. Yuan, Y. Zengquan, H. Rongzu, J. Therm. Anal. Cal. 58 (1999) 369–373.
[7] H.E. Kissinger, Anal. Chem. 29 (11) (1957) 1702–1706.
[8] N. Binke, L. Rong, Y. Zhengquan, H. Rongzu, Y. Qingsen, Hanneng Cailiao 7 (4) (1999) 162–165.
[9] N. Eisenreich, A. Pfeil, Thermochim. Acta 61 (1–2) (1983) 13.
[10] N. Eisenreich, Doctorate Dissertation, Technical University of Munich, 1978.