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The estimation of critical temperatures of thermal explosion for energetic materials using non-isothermal DSC

Zhang Tonglai [a], Hu Rongzu [b,*], Xie Yi [b], Li Fuping [b]

[a] *Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China*

[b] *Xian Modern Chemistry Research Institute, Xian 710061, Shaanxi, People's Republic of China*

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Abstract

A method for estimating critical temperatures (T_b) of thermal explosion for energetic materials is derived from Semenov's thermal explosion theory and the non-isothermal kinetic equation $d\alpha/dt = Af(\alpha)e^{-E/RT}$ using reasonable hypotheses. The final formula is simple: $E(T_b - T_{i0}) - RT_b^2 = 0$. We can easily obtain the values of the thermal decomposition activation energy (E) and the onset temperature (T_i) from the non-isothermal DSC curves of any kind of energetic materials, and then calculate the critical temperature (T_b) of thermal explosion. The results obtained with this method coincide very well with the measured values for the common explosives HMX, RDX, Tetryl, and NTO as well as its ethylenediammonium salt (ENTO), potassium salt (KNTO), lead salt (PbNTO) and copper salt (CuNTO).

Keywords: Critical temperature; DSC; Explosive; Non-isothermal; Stability

1. Introduction

The critical temperature (T_b) of thermal explosion is a very important parameter for energetic materials. Much research has been done in this area [1,2]. Here we describe a method for estimating the value of T_b using non-isothermal DSC curves

* Corresponding author.

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of any kind of energetic materials. This method is comparatively simple and economical; the required data can be obtained by non-isothermal DSC measurement alone, and the results obtained coincide very well with those of other methods [2–5].

2. Theoretical

For most energetic materials, their enthalpy of thermal decomposition reaction per unit time can be expressed by the equation

$$q_1 = Q\frac{Vd}{M}\frac{d\alpha}{dt} \tag{1}$$

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

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \tag{2}$$

where A is the pre-exponential factor in s^{-1}, E is the activation energy of the thermal decomposition reaction in J mol^{-1}, α is the reacted percent of energetic materials, and T is the reaction temperature in K.

Substituting $d\alpha/dt$ in Eq. (1) with Eq. (2), the expression for q_1 becomes

$$q_1 = Q\frac{Vd}{M}Af(\alpha)e^{-E/RT} \tag{3}$$

with linear increase in temperature

$$T = T_0 + \phi t \tag{4}$$

where ϕ is the heating rate in K min^{-1}, T_0 is the initial temperature of the reaction system in K, t is the heating time in s^{-1}, T is the temperature of the reaction system at time t in K.

Therefore, it is apparent that the enthalpy of thermal decomposition q_1 is proportional to the exponent of the reciprocal of reaction temperature T. At the same time, the heat (q_2) lost from the reaction system in unit time may be expressed

$$q_2 = \beta S(T - T_s) \tag{5}$$

where β is an overall heat transfer coefficient in J cm^{-2} K^{-1} s^{-1}, S is the external surface area of the loaded sample in cm^2, T is the temperature of the reaction system in K, T_s is the surrounding temperature in K, which is determined by the linear temperature increase in DSC analysis.

With the boundary conditions of thermal explosion, Eq. (3) becomes

$$q_1|_{T_b} = Q\frac{Vd}{M}Af(\alpha_b)e^{-E/RT_b} \tag{6}$$

and Eq. (5) becomes

$$q_2|_{T_b} = \beta S(T_b - T_{sb}) \tag{7}$$

where T_{sb} is the surrounding temperature at the beginning of the thermal explosion in K.

According to Semenov's thermal explosion theory [6], the sufficient and essential conditions from thermal decomposition to thermal explosion might be expressed as

$$\begin{cases} q_1|_{T_b} = q_2|_{T_b} & (8) \\ \left.\dfrac{dq_1}{dT}\right|_{T_b} = \left.\dfrac{dq_2}{dT}\right|_{T_b} & (9) \end{cases}$$

Differentiating Eq. (3) with respect to T, and considering Eq. (4), we obtain

$$\left.\frac{dq_1}{dT}\right|_{T=T_b,\alpha=\alpha_b} = \frac{1}{(dT/dt)_{T_b}} \frac{QVd}{M} Af(\alpha_b)e^{-E/RT_b} \left[Af'(\alpha_b)e^{-E/RT_b} + \frac{E}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right] \tag{10}$$

Differentiating Eq. (5) with respect to T, and considering Eq. (4), we obtain

$$\left.\frac{dq_2}{dT}\right|_{T=T_b} = \frac{1}{(dT/dt)_{T_b}} \beta S\left[\left(\frac{dT}{dt}\right)_{T_b} - \phi\right] \tag{11}$$

Combining Eqs. (6), (7), and (8)

$$\frac{QVd}{M} Af(\alpha_b)e^{-E/RT_b} = \beta S(T_b - T_{sb}) \tag{12}$$

Combining Eqs. (9), (10), and (11)

$$\frac{QVd}{M} Af(\alpha_b)e^{-E/RT_b}\left[Af'(\alpha_b)e^{-E/RT_b} + \frac{E}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right] = \beta S\left[\left(\frac{dT}{dt}\right)_{T_b} - \phi\right] \tag{13}$$

Combining Eqs. (12) and (13)

$$\left[Af'(\alpha_b)e^{-E/RT_b} + \frac{E}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right](T_b - T_{sb}) = \left(\frac{dT}{dt}\right)_{T_b} - \phi \tag{14}$$

For most explosives, the differential form of the mechanism function for the thermal decomposition reaction may be expressed as $f(\alpha) = (1 - \alpha)^n$ and when the transition from thermal decomposition to thermal explosion is triggered, the fraction of the material reacted α is very small, i.e. $f(\alpha) \approx 1$ and $f'(\alpha) = 0$. Equation (14) may therefore be expressed as

$$\frac{E}{RT_b^2}(T_b - T_{sb}) = \frac{(dT/dt)_{T_b} - \phi}{(dT/dt)_{T_b}} \tag{15}$$

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

When the transition from thermal decomposition to thermal explosion begins, the surrounding temperature is near to the onset temperature T_i of the DSC curve.

Substituting T_i of the DSC curves with heating rate ϕ_i for T_{sb}, when ϕ tends to zero, we take the limitation of both sides of Eq. (15)

$$\lim_{\phi \to 0} \frac{E}{RT_b^2}(T_b - T_{sb}) = \lim_{\phi \to 0} \frac{E}{RT_b^2}(T_b - T_i) = \frac{E}{RT_b^2}(T_b - T_{i0}) \tag{16}$$

$$\lim_{\phi \to 0} \frac{(\mathrm{d}T/\mathrm{d}t)_{T_b} - \phi}{(\mathrm{d}T/\mathrm{d}t)_{T_b}} = 1 \tag{17}$$

Therefore, Eq. (15) can be simplified into the form

$$\frac{E}{RT_b^2}(T_b - T_{i0}) = 1 \tag{18}$$

It may also be expressed as

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{i0}}}{2R} \tag{19}$$

Because the root of Eq. (18) is unreasonable, it is omitted.

The value of T_{i0} corresponding to $\phi = 0$ may be obtained by using linear regression of T_i and ϕ_i as described in Eq. (20)

$$T_i = a + b\phi_i + c\phi_i^2 + d\phi_i^3 \tag{20}$$

The value of T_i is easily obtained from the DSC curve with the heating rate ϕ_i, and a unique equation set can be defined using four groups of T_i and ϕ_i. When ϕ tends to zero, the value of T_i equals the value of a, and it is designated T_{i0}. The value of the activation energy E may be obtained using the same DSC analyses with the Ozawa method [7], which is unrelated to the mechanism function, or with the Kissinger method [8] which mainly concerns the mechanism function as $f(\alpha) = (1 - \alpha)^n$.

3. Experimental

3.1. Materials

The HMX, RDX and Tetryl used in these experiments were all commercial products. NTO and its ethylenediammonium salt (ENTO), potassium salt (KNTO), lead salt (PbNTO) and copper salt (CuNTO) were all freshly prepared and purified.

3.2. Instruments 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 (5 mm in diameter, 3 mm high), whose side is rolled up with a lid. The conditions of the DSC analyses were: sample mass, <1 mg; heating rates, 1, 2, 5, 10 and 20 K min^{-1}, respectively; calorimetric sensitivities, ± 10.5 and ± 20.9 mJ s^{-1}, respectively; atmosphere, self-generating; reference sample, α-Al_2O_3. The other instruments and conditions used were as described in our previous paper [2].

4. Results and discussion

The calculations of Eqs. (19) and (20) were carried out on a personal computer programmed in FORTRAN. The activation energy E of the thermal decomposition was first derived by Ozawa's method [7] using the DSC analysis results. Then the values of the coefficients of Eq. (20) were solved using the onset temperature and heating rates obtained from the same DSC analyses. Finally, the value of the

Table 1
The initial data and the obtained values of T_{i0} and E

Sample	ϕ_i/K min^{-1}	T_i/K	T_{i0}/K	T_m/K [a]	E/kJ mol^{-1} [b]
HMX	1	537	534.2	538	380.9
	5	545		548	
	11	550		551	
	23	557		558	
RDX	2	473	468.1	485	134.7
	5	480		497	
	10	490		508	
	23	499		521	
Tetryl	2	451	442.3	467	176.7
	5	460		475	
	11	468		486	
	22	476		490	
NTO	1	537	533.9	539	504.1
	2	539		540	
	5	541		544	
	10	545		549	
ENTO	1	502	490.5	504	206.5
	2	510		512	
	5	519		522	
	11	524		528	
KNTO	1	501	488.6	503	190.8
	2	510		513	
	5	520		523	
	22	535		538	
PbNTO	1	469	465.4	479	244.8
	2	472		485	
	10	482		496	
	20	488		503	
CuNTO	1	479	450.6	515	118.9
	2	498		527	
	5	510		542	
	20	531		574	

[a] T_m is the maximum temperature of the peak. [b] E values obtained using Ozawa's method [7].

Table 2
The calculated results of T_b compared with published data

	HMX	RDX	Tetryl	NTO	ENTO	KNTO	PbNTO	CuNTO
T_b/K [a]	541	482	452	539	501	499	473	466
T_b/K [b]	529	488	473	513	497	491	472	463
T_b/K [c]				521	489	495	454	475
T_b/K [d]				530	518	496	480	
R.E./% [e]	2.3	1.2	4.4	5.1	0.8	1.6	0.2	0.6

[a] Calculated using the present method. [b] Cited from Ref. 2, using a method described in Ref. 2. [c] Cited from Ref. 2, obtained using the Frank-Kamenetskii method. [d] Cited from Ref. 2, using the Zinn–Mader–Roger method. [e] Relative error of T_b^a and T_b^b.

critical temperature of thermal explosion was obtained from Eq. (19) using these parameters of E, T_{i0} and R (8.314 J mol^{-1} K^{-1}).

The initial data used for calculating T_{i0} and activation energy E are shown in Table 1 together with the T_{i0} and E results obtained. The calculated results of T_b are shown in Table 2. It is clear that the values of T_b calculated using this method coincide very well with the measured values [2]. If the exothermic peak on the DSC curve of the energetic material is not too steep to be measured accurately, as for RDX, ENTO, KNTO, PbNTO and CuNTO, the relative error of the values of T_b calculated with this method relative to those measured is less than 2%.

5. Conclusions

The T_b results obtained with this method are reasonable. The error is mainly caused by the inaccuracy of the measurements. The relative error values are usually less than 5% for these samples. Therefore, it can be concluded that this method may be used for estimating the critical temperature of thermal explosion for energetic materials.

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