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ESTIMATION OF THE CRITICAL TEMPERATURE OF THERMAL EXPLOSION FOR AZIDO-ACETIC-ACID-2-(2-AZIDO-ACETOXY)-ETHYLESTER USING NON-ISOTHERMAL DSC

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A method for estimating the critical temperatures (T_b) of thermal explosion for energetic materials is derived from Semenov's thermal explosion theory and the non-isothermal kinetic equation $\mathrm{d}\alpha/\mathrm{d}t=A_0T^{\mathrm{B}}f(\alpha)\mathrm{e}^{-\mathrm{E/RT}}$ using reasonable hypotheses. The final formula of calculating the value of T_b is $\left(\frac{B}{T_\mathrm{b}}+\frac{E}{RT_\mathrm{b}^2}\right)(T_\mathrm{b}-T_\mathrm{e0})=1$. The data needed for the method, E and T_e0, can be obtained from analyses of the non-isothermal DSC curves. When B=0.5 the critical temperature (T_b) of thermal explosion of azido-acetic-acid-2-(2-azido-acetoxy)-ethylester (EGBAA) is determined as 475.65 K.

Keywords: *azido-acetic-acid-2-(2-azido-acetoxy)-ethylester (EGBAA), critical temperature, decomposition, kinetic parameters, Kooij's equation, thermal explosion*

Introduction

Azido-acetic-acid-2-(2-azido-acetoxy)-ethylester (EGBAA) is of interest because it has good compatibility with azido binders, also has azido groups as similar structural elements to improve the mechanical properties of azido binders for propellants. Besides a good compatibility, EGBAA would have the advantage of delivering extra energy on combustion combined with minimum smoke. During their exothermic decomposition it exclusively gives smokeless burning products with a high amount of nitrogen. Its density is 1.34 g cm^{-3} (25°C). Its heat of detonation is 1065J g^{-1}. Its synthesis [1] and characterization [2] have been reported. In the present work, we report its kinetic parameters of the exothermic decomposition reaction studied with DSC and describe a method based on Kooij equation for estimating the value of T_b using non-isothermal DSC curves. In comparison with calculating activation energy (E) and pre-exponential facter (A) in [3], we use the non-isothermal kinetic equation $\mathrm{d}\alpha/\mathrm{d}t=A_0T^{\mathrm{B}}f(\alpha)e^{-\mathrm{E/RT}}$ based on Kooij equation. In comparison with the method of estimating self-heating rate ($\mathrm{d}T/\mathrm{d}t$) [4], this method of estimating the value of T_b is comparatively simple and the required data can be obtained by non-isothermal DSC measurement alone. A typical calculation for azido-acetic-acid-2-(2-azido-acetoxy)-ethylester (EGBAA) is given.

Theory and method

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

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

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 cm^{-1}, M is the mole mass of explosive loaded in g and $\mathrm{d}\alpha/\mathrm{d}t$ is the reaction rate which may be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha)=A_0T^{\mathrm{B}}f(\alpha)e^{-\mathrm{E/RT}} \tag{2}$$

where

$$k=A_0T^{\mathrm{B}}\mathrm{e}-^{\mathrm{E/RT}} \tag{3}$$

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

$$q_1=Q\frac{Vd}{M}A_0T^{\mathrm{B}}f(\alpha)\mathrm{e}^{-\mathrm{E/RT}} \tag{4}$$

with linear increase in temperature (Eq. (5)).

$$T=T_0+\beta t \tag{5}$$

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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

$$q_2=kS(T-T_s) \tag{6}$$

where k 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. (4) becomes

$$q_1\big|_{T_b}=Q\frac{Vd}{M}A_0T_b^{B}f(\alpha)e^{-E/RT_b} \tag{7}$$

and Eq. (6) becomes

$$q_2\big|_{T_b}=kS(T_b-T_{sb}) \tag{8}$$

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

According to Semenov's thermal explosion theory [5], the sufficient and essential conditions from thermal decomposition to thermal explosion are

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

$$\frac{dq_1}{dT}\bigg|_{T_b}=\frac{dq_2}{dT}\bigg|_{T_b} \tag{10}$$

Differentiating Eq. (4) with respect to T and considering Eq. (5), give Eq. (11).

$$\frac{dq_1}{dT}\bigg|_{T_b}=\frac{1}{(dT\text{–}dt)_{T_b}}\frac{QVdT_b^{B}}{M}A_0f(\alpha_b)e^{-E/RT}\left[\frac{B}{T_b}\left(\frac{dT}{dt}\right)_{T_b}+A_0f'(\alpha)e^{-E/RT}+\frac{E}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right] \tag{11}$$

Differentiating Eq. (6) with respect to T and considering Eq. (5), yield Eq. (12).

$$\frac{dq_1}{dT}\bigg|_{T_b}=\frac{1}{(dT\text{–}dt)_{T_b}}kS\left[\left(\frac{dT}{dt}\right)_{T_b}-\beta\right] \tag{12}$$

Combining Eqs (7–9), yield Eq. (13).

$$Q\frac{Vd}{M}A_0T_b^{B}f(\alpha_b)e^{-E/RT_b}=ks(T_b-T_{sb}) \tag{13}$$

Combining Eqs (10), (11) and (12), yield Eq. (14).

$$\frac{QVdT_b^{B}}{M}A_0f(\alpha_b)e^{-E/RT}\left[\frac{B}{T_b}\left(\frac{dT}{dt}\right)_{T_b}+A_0f'(\alpha)e^{-E/RT}+\frac{E}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right]=kS\left[\left(\frac{dT}{dt}\right)_{T_b}-\beta\right] \tag{14}$$

Combining Eqs (13) and (14), yield Eq. (15).

$$\left[\frac{B}{T_b}\left(\frac{dT}{dt}\right)_{T_b}+A_0f'(\alpha)e^{-E/RT}+\frac{E}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right](T_b-T_{sb})=\left(\frac{dT}{dt}\right)_{T_b}-\beta \tag{15}$$

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. $f(\alpha)\approx1$ and $f'(\alpha)=0$. Equation (15) may therefore be expressed as

$$\left(\frac{B}{T_b}+\frac{E}{RT_b^2}\right)(T_b-T_{sb})=\frac{\left(\frac{dT}{dt}\right)_{T_b}-\beta}{\left(\frac{dT}{dt}\right)_{T_b}} \tag{16}$$

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_e of the DSC curve. Substituting T_{ei} of DSC curves with heating rate β_i for T_{sb}, when β tends to zero, we take the limitation of both sides of Eq. (16)

$$\lim_{\beta\to0}\left(\frac{B}{T_b}+\frac{E}{RT_b^2}\right)(T_b-T_{sb})=\lim_{\beta\to0}\left(\frac{B}{T_b}+\frac{E}{RT_b^2}\right)(T_b-T_e)=\left(\frac{B}{T_b}+\frac{E}{RT_b^2}\right)(T_b-T_{e0}) \tag{17}$$

$$\lim_{\beta\to0}\frac{\left(\frac{dT}{dt}\right)_{T_b}-\beta}{\left(\frac{dT}{dt}\right)_{T_b}}=1 \tag{18}$$

Therefore, Eq. (16) can be simplified into the form

$$\left(\frac{B}{T_b}+\frac{E}{RT_b^2}\right)(T_b-T_{e0})=1 \tag{19}$$

It may also be expressed as

$$T_\mathrm{b}=\frac{E-\sqrt{E^2-4R(1-B)(BR+E)T_\mathrm{e0}}}{2R(1-B)} \tag{20}$$

Substituting B=0 into Eq. (20) gives Zhang–Hu–Xie–Li's formula

$$T_\mathrm{b}=\frac{E-\sqrt{E^2-4RET_\mathrm{e0}}}{2R} \tag{21}$$

showing that Eq. (20) includes Eq. (21).

The value of T_e0 corresponding to $\beta\to0$ may be obtained by using linear regression of T_ei and β_i as described in Eq. (22)

$$\begin{gathered}T_\mathrm{ei}=T_\mathrm{e0}+a_1\beta_\mathrm{i}+a_2\beta_\mathrm{i}^2+a_3\beta_\mathrm{i}^3+...+a_{\mathrm{L}-2}\beta_\mathrm{i}^{\mathrm{L}-2}\\ i=1,2,3,...,L\end{gathered} \tag{22}$$

The value of T_e is easily obtained from the DSC curve with the heating rate β_i, and a unique equation set can be defined using four groups or five groups of T_ei and β_i. When β tends to zero, the value of T_e0 equals the value of a_0, and it is designated T_e0.

The integral isoconversional non-isothermal kinetic equation based on Kooij equation is

$$G(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}T^\mathrm{B}(T-T_0)\exp(-E/RT) \tag{23}$$

at same α,

$$\begin{aligned}&\frac{A}{\beta_1}T_{\alpha,1}^\mathrm{B}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})=\\ &\frac{A}{\beta_2}T_{\alpha,2}^\mathrm{B}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})=\\ &\frac{A}{\beta_\mathrm{n}}T_{\alpha,\mathrm{n}}^\mathrm{B}(T_{\alpha,\mathrm{n}}-T_{0,\mathrm{n}})\exp(-E_\alpha/RT_{\alpha,\mathrm{n}})\end{aligned} \tag{24}$$

Finally, Eq. (24) leads to

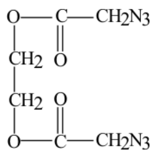
$$\begin{gathered}\Omega_\mathrm{KI}(E_\alpha)=\\ =\min\sum_{\mathrm{i}=1}^{\mathrm{n}}\sum_{\mathrm{j}\neq\mathrm{i}}^{\mathrm{n}}\frac{\beta_\mathrm{j}T_{\alpha,\mathrm{i}}^\mathrm{B}(T_{\alpha,\mathrm{i}}-T_{0,\mathrm{i}})\exp(-E_\alpha/RT_{\alpha,\mathrm{i}})}{\beta_\mathrm{i}T_{\alpha,\mathrm{j}}^\mathrm{B}(T_{\alpha,\mathrm{j}}-T_{0,\mathrm{j}})\exp(-E_\alpha/RT_{\alpha,\mathrm{j}})}-\\ -n(n-1)\end{gathered} \tag{25}$$

This method of calculating the E_a value is named for NL-INT-B method. By substituting experimental the values of β_i, T_i, T_0i, n obtained from an analysis of the DSC or DTG curve into Eq. (25) and varying E_α to reach the minimum, gives the value of E_α at a given degree of conversion.

Experimental

Materials

EGBAA used in this work (Scheme 1) was prepared and purified at Xi'an Modern Chemistry Research Institute. Its purity is more than 99.0%. The structure of EGBAA was characterized by elemental analyses, IR spectrometry, mass spectrometry and unclear magnetic resonance spectrometry. The sample was kept in a vacuum desiccator before use.



Scheme 1

Instruments and conditions

The thermal decomposition process of EGBAA under the condition of flowing N_2 gas was studied on a TG and DSC apparatus (TA, USA). The conditions of TG were as follows: sample mass, ca. 0.5 mg; heating rate, 10°C min^{-1}; atmosphere, a flowing rate of N_2 gas of 120 mL min^{-1}; reference sample, α-Al_2O_3. The conditions of DSC were as follows: sample mass, ca, 1 mg; heating rates, 5, 10, 15, 20, 30 and 40 K min^{-1}; atmosphere, a flowing rate of N_2 gas of 60 mL min^{-1}; reference sample, α-Al_2O_3.

Results and discussion

By substituting the original data, β_i, T_i and α_i, i=1,2,...n, tabulated in Table 1 from DSC curves into Eq. (25), the values of E_α for any given value of α in Table 2 are obtained. The average value of E_α in the α range of 0.175 to 0.725 in Fig. 1 is 137.66 kJ mol^{-1}.

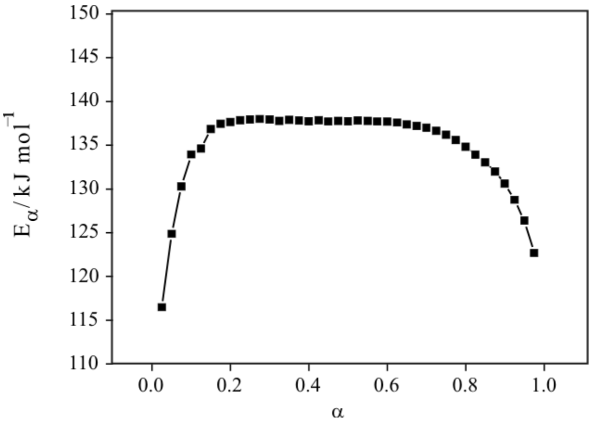


Fig. 1 E_α~α curves for the decomposition of EGBAA by NL-INT-B method

Table 1 Data of EGBAA determined by DSC

No.	α	T/K					
		β=5 K min^{-1}	β=10 K min^{-1}	β=15 K min^{-1}	β=20 K min^{-1}	β=30 K min^{-1}	β=40 K min^{-1}
1	0.025	470.25	483.75	483.65	488.25	494.05	503.76
2	0.050	477.25	490.75	491.05	497.25	500.85	509.96
3	0.075	481.95	495.05	496.15	502.35	505.47	514.17
4	0.100	485.55	498.25	499.75	505.95	509.09	517.45
5	0.125	488.25	500.95	502.75	508.85	512.09	520.35
6	0.150	490.65	503.15	505.15	511.25	514.66	522.51
7	0.175	492.65	505.10	507.25	513.35	516.92	524.58
8	0.200	494.40	506.85	509.10	515.25	518.94	526.44
9	0.225	496.00	508.40	510.75	516.95	520.79	528.13
10	0.250	497.45	509.80	512.25	518.45	522.47	529.69
11	0.275	498.80	511.15	513.60	519.87	524.04	531.14
12	0.300	500.05	512.35	514.85	521.20	525.50	532.49
13	0.325	501.20	513.50	516.05	522.45	526.87	533.77
14	0.350	502.35	514.55	517.15	523.60	528.17	534.97
15	0.375	503.40	515.55	518.20	524.70	529.39	536.12
16	0.400	504.40	516.50	519.21	525.73	530.56	537.21
17	0.425	505.39	517.40	520.20	526.70	531.67	538.26
18	0.450	506.30	518.25	521.10	527.61	532.74	539.27
19	0.475	507.20	519.05	522.00	528.47	533.76	540.23
20	0.500	508.05	519.85	522.85	529.28	534.73	541.17
21	0.525	508.90	520.60	523.65	530.07	535.67	542.07
22	0.550	509.70	521.33	524.45	530.83	536.58	542.95
23	0.575	510.48	522.05	525.22	531.57	537.45	543.82
24	0.600	511.25	522.75	525.99	532.28	538.30	544.68
25	0.625	511.99	523.45	526.75	532.95	539.14	545.53
26	0.650	512.70	524.15	527.48	533.61	539.97	546.37
27	0.675	513.42	524.83	528.21	534.26	540.79	547.22
28	0.700	514.15	525.51	528.95	534.95	541.61	548.07
29	0.725	514.85	526.20	529.69	535.66	542.43	548.94
30	0.750	515.55	526.91	530.45	536.38	543.26	549.83
31	0.775	516.25	527.60	531.22	537.13	544.10	550.76
32	0.800	516.95	528.32	532.02	537.91	544.98	551.73
33	0.825	517.70	529.09	532.87	539.02	545.88	552.76
34	0.850	518.45	529.85	533.76	539.58	546.83	553.88
35	0.875	519.30	530.70	534.75	540.52	547.84	555.13
36	0.900	520.20	531.65	535.85	541.56	548.94	556.56
37	0.925	521.25	532.75	537.15	542.77	550.19	558.32
38	0.950	522.60	534.20	538.75	544.27	551.70	560.65
39	0.975	524.65	536.45	541.25	546.46	553.82	564.35

The measured values of β_i, T_{ei}, the calculated value of E from Eq. (25) and the obtained values of T_{e0} when β tends to zero, together with reasonable values of T_b obtained by substituting the above-mentioned values into Eq. (20), are shown in Table 3.

The calculated results of T_b using this method is 3% less than that obtained by Zhang–Hu–Xie–Li method. Therefore, it can be concluded that this method is tenable for estimating the critical temperature of

Table 2 Apparent activation energies of thermal decomposition of EGBAA obtained using isoconversional methods [Eq. (25)] and the data taken from Table 1

No.	α	E_α/kJ mol^{-1}	No.	α	E_α/kJ mol^{-1}
1	0.025	116.48	21	0.525	137.82
2	0.050	124.87	22	0.550	137.78
3	0.075	130.30	23	0.575	137.73
4	0.100	133.94	24	0.600	137.70
5	0.125	134.61	25	0.625	137.61
6	0.150	136.85	26	0.650	137.40
7	0.175	137.45	27	0.675	137.20
8	0.200	137.66	28	0.700	137.02
9	0.225	137.86	29	0.725	136.64
10	0.250	137.96	30	0.750	136.21
11	0.275	138.01	31	0.775	135.59
12	0.300	137.95	32	0.800	134.81
13	0.325	137.76	33	0.825	133.93
14	0.350	137.91	34	0.850	133.02
15	0.375	137.81	35	0.875	131.99
16	0.400	137.74	36	0.900	130.59
17	0.425	137.86	37	0.925	128.76
18	0.450	137.71	38	0.950	126.39
19	0.475	137.77	39	0.975	122.67
20	0.500	137.75			

mean in the range of 0.175 to 0.725: $E_{\alpha=0.175\sim0.725}$=137.66 kJ mol^{-1}

Table 3 The critical temperature of thermal explosion of EGBAA

β_i/K min^{-1}	T_{ei}/K	T_{e0}/K	this work (B=0.5)		Zhang–Hu–Xie–Li method [6]		
			E^*/kJ mol^{-1}	T_b/K	E_0^{**}/kJ mol^{-1}	r	T_b/K
5	484.55	468.8	137.66	475.65	130.01	0.9947	491.07
10	496.55						
15	500.75						
20	507.45						
30	510.75						
40	516.55						

*$E=E_\alpha$, **value of E_0 calculated from the relationship of β_i *vs*. $1/T_{ei}$ (Ozawa's method)

thermal explosion for energetic materials from the point of the safety evaluation.

Conclusions

A new method derived by Semenov's thermal explosion theory and the non-isothermal kinetic equation $d\alpha/dt=A_0T^Bf(\alpha)e^{-E/RT}$ is proposed for estimation of critical temperature of thermal explosion for energetic materials. The T_b result obtained with this method is 3% less than that obtained by Zhang–Hu–Xie–Li method. Therefore, it can be concluded that this method is more suited for estimating the critical temperature of thermal explosion for energetic materials from the point of the safety evaluation. For EGBAA, the apparent activation energy of the exothermic decomposition reaction obtained by using the integral isoconversional non-isothermal kinetic equation based on Kooij equation with B=0.5 is 137.66 kJ mol^{-1} and the critical temperature of thermal explosion is 475.65 K.

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