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## Estimation of Critical Temperature of Thermal Explosion for Some Furazano-fused Cyclic Compounds Using Non-isothermal DSC

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**Abstract:** Two general expressions and their six derived formulae for estimating the critical temperature ( $T_b$ ) of thermal explosion for energetic materials (EMs) are derived from the Semenov's thermal explosion theory and eight non-isothermal kinetic equations, using reasonable hypothesis. The initial temperature ( $T_{0i}$ ) at which DSC curve deviates from the baseline, the onset temperature ( $T_{ei}$ ), the kinetic parameters of exothermic decomposition reaction can be obtained from the non-isothermal DSC curve of EMs. The values of  $T_{00}$  and  $T_{e0}$  was obtained from the equation  $T_{0i \text{ or } ei} = T_{00 \text{ or } e0} + a_1\beta_i + a_2\beta_i^2 + \dots + a_{L-2}\beta_i^{L-2}$ ,  $i = 1, 2, \dots, L$  and then the values of  $T_b$  was calculated by the six derived formulae. The  $T_b$  results obtained with the six derived formulae for 1, 4, 5, 8-tertinitro-1, 4, 5, 8-tetraazadifurazano[3,4-c;3',4'-h] decalin and its parent compound, 1,3,4-trinitro-imidazolone[4,5-b] furazano[3,4-e] piperazine and its parent compound, 1,3,4,8-tetranitro-imidazolone[4,5-b] furazano[3,4-e] piperazine, 1,4,5,8- tetranitro -1,4,5,8-tetraza furazano[3,4-b] decalin and 1,3,5-trinitro-1,3,5-triazafurazano[3,4-f] cycloheptane approximate well to each other.

**Key words:** physical chemistry; furazano-fused cyclic compounds; critical temperature; thermal explosion; non-isothermal DSC

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### 1 Introduction

The critical temperature ( $T_b$ ) of thermal explosion is a very important parameter for energetic materials (EMs). Much research has been done in this area<sup>[1-13]</sup>. In the present work, we present two general expressions and their six derived formulae for estimating the critical temperature of thermal explosion for EMs, and report the values of  $T_b$  of 1, 4, 5, 8-tertinitro-1, 4, 5, 8-tetraazadifurazano[3,4-c;3',4'-h] decalin (I) and its parent compound (II), 1, 3, 4-trinitro-imidazolone[4,5-b] furazano[3,4-e] piperazine (III) and its parent compound (IV), 1, 3, 4, 8-tetranitro-imidazolone[4,5-b] furazano[3,4-e] piperazine (V), 1,4,5,8- tetranitro -1,4,5,8-tetraza furazano[3,4-b] decalin (VI) and 1,3,5-

trinitro-1,3,5-triazafurazano[3,4-f] cycloheptane (VII). The data needed for the six derived formulae can be obtained by the non-isothermal DSC measurement alone.

### 2 Theory and method

#### 2.1 Derivation of general expression with the initial temperature $T_0$ for estimating the value of $T_b$

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

$$q_1 = Q \frac{V\rho}{M} \frac{d\alpha}{dt} \quad (1)$$

where  $Q$  is the enthalpy of the thermal decomposition reaction in  $\text{J} \cdot \text{mol}^{-1}$ ;  $V$  is the volume of explosive loaded in  $\text{cm}^3$ ;  $\rho$  is the loading density in  $\text{g} \cdot \text{cm}^{-3}$ ;  $M$  is the mole mass of explosive loaded in  $\text{g}$  and  $\frac{d\alpha}{dt}$  is the reaction rate which may be expressed as Eq. (2)

$$\frac{d\alpha}{dt} = A_0 T^a \exp\left[bT - \frac{dE}{R(T+c)}\right] \times \left\{1 + (T - T_0) \left[\frac{a}{T} + \left[b + \frac{dE}{R(T+c)^2}\right]\right]\right\} f(\alpha) \quad (2)$$

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

$$q_1 = Q \frac{V\rho}{M} A_0 T^a \exp\left[bT - \frac{dE}{R(T+c)}\right] \times \left\{1 + (T - T_0) \left[\frac{a}{T} + \left[b + \frac{dE}{R(T+c)^2}\right]\right]\right\} f(\alpha) \quad (3)$$

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

$$q_2 = k' S (T - T_s) \quad (4)$$

where  $k'$  is an overall heat transfer coefficient in  $J \cdot cm^{-2} \cdot K^{-1} \cdot s^{-1}$ ;  $S$  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

$$\frac{dq_1}{dT} \Big|_{T_b} = \frac{QV\rho}{M} A_0 a T_b^a \exp\left[bT_b - \frac{dE}{R(T_b+c)}\right] \cdot \left[1 + (T_b - T_0) \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right]\right] \times \left\{ \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right] + \frac{\left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right] + (T_b - T_0) \left[-\frac{a}{T_b^2} - \frac{2dE}{R(T_b+c)^3}\right]}{1 + (T_b - T_0) \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right]} \right\} \quad (9)$$

Differentiating Eq. (4) with respect to  $T$  and considering Eq. (5), yield Eq. (10).

$$\frac{dq_2}{dT} \Big|_{T_b} = \frac{1}{(dT/dt)_{T_b}} k' S \left[ \left(\frac{dT}{dt}\right)_{T_b} - \beta \right] \quad (10)$$

Combining Eqs. (5), (6) and (7), yields Eq. (11).

$$Q \frac{V\rho}{M} A_0 T_b^a \exp\left[bT_b - \frac{dE}{R(T_b+c)}\right] \left\{1 + (T_b - T_0) \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right]\right\} f(\alpha) = k' S (T_b - T_{sb}) \quad (11)$$

Combining Eqs. (8), (9) and (10), yields Eq. (12).

$$\frac{QV\rho}{M} A_0 a T_b^a \exp\left[bT_b - \frac{dE}{R(T_b+c)}\right] \cdot \left[1 + (T_b - T_0) \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right]\right] \times \left\{ \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right] + \frac{\left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right] + (T_b - T_0) \left[-\frac{a}{T_b^2} - \frac{2dE}{R(T_b+c)^3}\right]}{1 + (T_b - T_0) \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right]} \right\} = \frac{1}{(dT/dt)_{T_b}} k' S \left[ \left(\frac{dT}{dt}\right)_{T_b} - \beta \right] \quad (12)$$

Combining Eqs. (11) and (12), yields Eq. (13).

$$(T_b - T_{sb}) \left\{ \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right] + \frac{\left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right] + (T_b - T_0) \left[-\frac{a}{T_b^2} - \frac{2dE}{R(T_b+c)^3}\right]}{1 + (T_b - T_0) \left[\frac{a}{T_b} + \left[b + \frac{dE}{R(T_b+c)^2}\right]\right]} \right\} = \frac{1}{(dT/dt)_{T_b}} \left[ \left(\frac{dT}{dt}\right)_{T_b} - \beta \right] \quad (13)$$

$$q_1 \Big|_{T_b} = Q \frac{V\rho}{M} A_0 T_b^a \exp\left[bT - \frac{dE}{R(T+c)}\right] \times \left\{1 + (T - T_0) \left[\frac{a}{T} + \left[b + \frac{dE}{R(T+c)^2}\right]\right]\right\} f(\alpha) \quad (5)$$

and Eq. (4) becomes

$$q_2 \Big|_{T_b} = k' S (T_b - T_{sb}) \quad (6)$$

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

The condition of thermal explosion formulated by Semenov<sup>[14]</sup> is the equality heat liberation  $q_1$  and heat transmission  $q_2$ :

$$q_1 \Big|_{T_b} = q_2 \Big|_{T_b} \quad (7)$$

$$\left. \frac{dq_1}{dT} \right|_{T_b} = \left. \frac{dq_2}{dT} \right|_{T_b} \quad (8)$$

Differentiating Eq. (3) with respect to  $T$  and considering constant heating rate ( $\beta$ ) equation,  $T = T_0 + \beta t$  and for most explosives, the differential mechanism function for the thermal decomposition reaction is  $f(\alpha) = (1 - \alpha)^n$ , since thermal explosion starts in range of low decomposition degrees,  $(1 - \alpha)^n \rightarrow 1$ ,  $f'(\alpha) = 0$ , give Eq. (9).

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  $\beta_i$  for  $T_{sb}$ , when  $\beta$  tends to zero, we take the limitation of both sides of Eq. (13)

$$\begin{aligned} & \lim_{\beta \rightarrow 0} (T_b - T_{sb}) \left\{ \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + \frac{\left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + (T_b - T_0) \left[ -\frac{a}{T_b^2} - \frac{2dE}{R(T_b + c)^3} \right]}{1 + (T_b - T_0) \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right]} \right\} \\ & = \lim_{\beta \rightarrow 0} (T_b - T_e) \left\{ \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + \frac{\left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + (T_b - T_0) \left[ -\frac{a}{T_b^2} - \frac{2dE}{R(T_b + c)^3} \right]}{1 + (T_b - T_0) \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right]} \right\} \\ & = (T_b - T_{e0}) \left\{ \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + \frac{\left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + (T_b - T_{00}) \left[ -\frac{a}{T_b^2} - \frac{2dE}{R(T_b + c)^3} \right]}{1 + (T_b - T_{00}) \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right]} \right\} \quad (14) \end{aligned}$$

$$\lim_{\beta \rightarrow 0} \frac{\left( \frac{dT}{dt} \right)_{T_b} - \beta}{\left( \frac{dT}{dt} \right)_{T_b}} = 1 \quad (15)$$

Therefore, Eq. (13) can be simplified into the form

$$(T_b - T_{e0}) \left\{ \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + \frac{\left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right] + (T_b - T_{00}) \left[ -\frac{a}{T_b^2} - \frac{2dE}{R(T_b + c)^3} \right]}{1 + (T_b - T_{00}) \left[ \frac{a}{T_b} + \left[ b + \frac{dE}{R(T_b + c)^2} \right] \right]} \right\} = 1 \quad (16)$$

Eq. (16) is the relation formula for estimating the critical temperature of thermal explosion of EMs when the exothermic decomposition reaction converts into thermal explosion.

Once the values of  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $T_{00}$ ,  $T_{e0}$  and  $E$  have been calculated from the heat flow curves, the corresponding value of  $T_b$  can then be obtained from Eq. (16).

## 2.2 Derivation of general expression without the initial temperature $T_0$ for estimating the value of $T_b$

Similarly, replacing Eq. (2) with Eq. (17),

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A_0 T^a \exp\left[ bT - \frac{dE}{R(T+c)} \right] f(\alpha) \quad (17)$$

one may obtain

$$(T_b - T_{e0}) \left[ \frac{a}{b} + b + \frac{dE}{R(T_b + c)^2} \right] = 1 \quad (18)$$

Eq. (18) is a general formula to estimate the critical temperature of thermal explosion of EMs without the initial temperature.

Once the values of  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $T_{e0}$  and  $E$  have been calculated from the heat flow curves, the corresponding value of  $T_b$  can then be obtained from Eq. (18).

## 2.3 Derivation of derived formulae for estimating the value of $T_b$

According to Eqs. (16) and (18), the simplified formulae (17)-(34) in Figs. 1 and 2 are obtained.

Once the values of  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $T_{00}$ ,  $T_{e0}$  and  $E$  have been calculated from the heat flow curves, the corresponding value of  $T_b$  can then be obtained from Eqs. (17) - (34).

## 2.4 Calculation of the value of $a$ , $b$ and $E$

Rearranging both sides of Eq. (2) and integrating between  $T_0$  and  $T$ , and the fraction of the material reacted between 0 and  $\alpha$ , yield Eq. (35).

According to Eq. (35), Eq. (36) and the simplified formula used to calculate the values of  $a$ ,  $b$  and  $E$  in Fig. 3 are obtained.

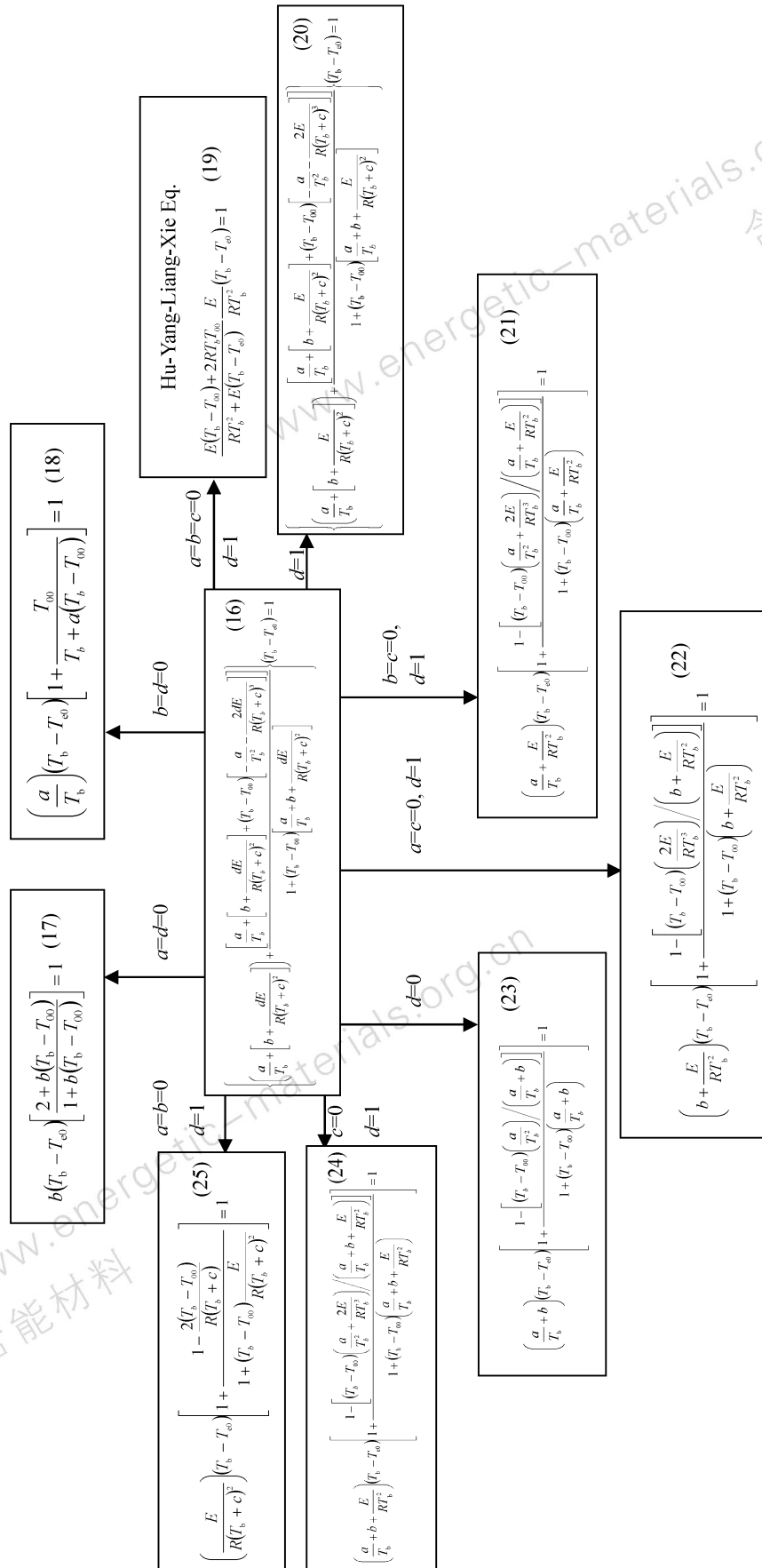


Fig. 1 Block diagram describing the relations among various formulae of computing the value of  $T_b$

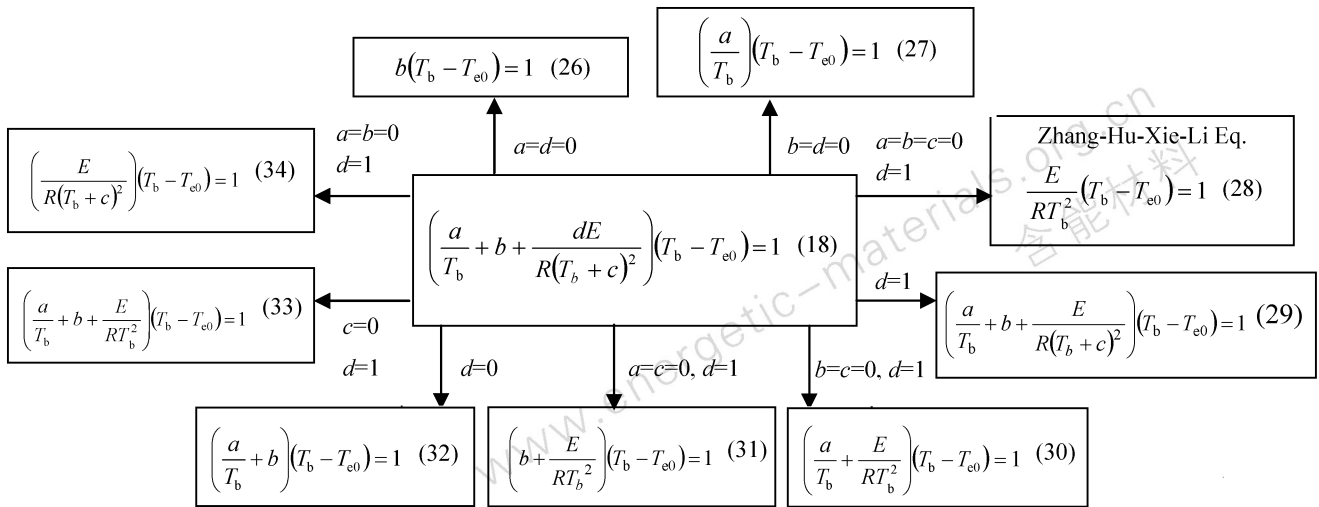


Fig. 2 Block diagram describing the relations among various formulae of computing the value of  $T_b$

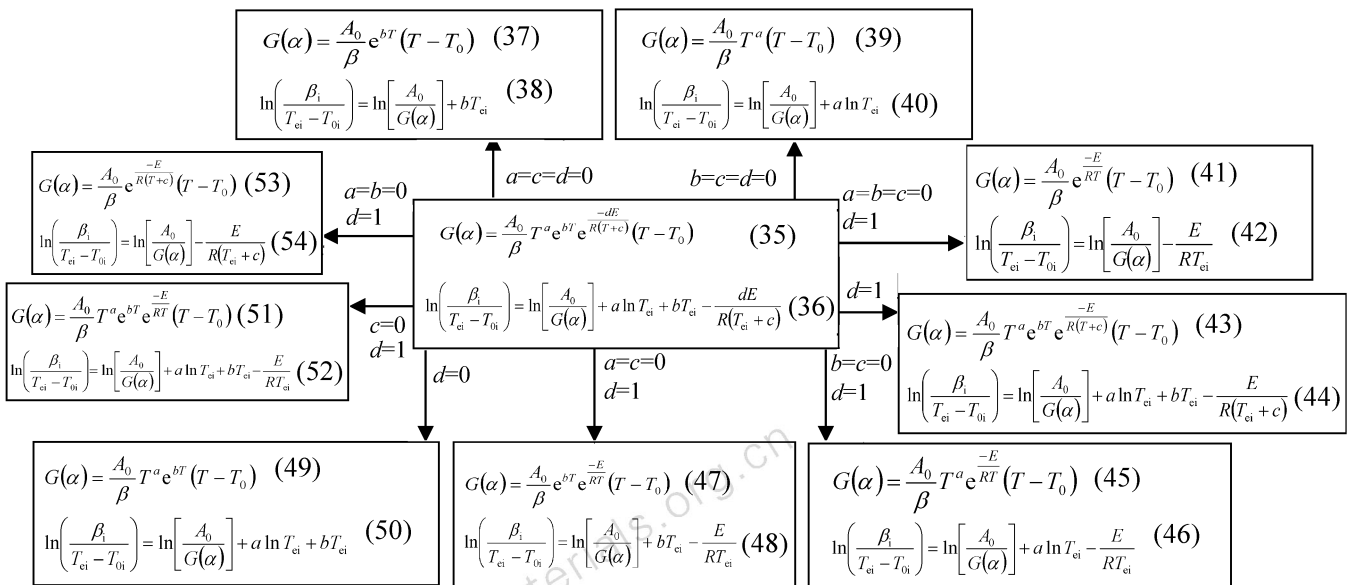


Fig. 3 Block diagram of various formulae describing the  $G(\alpha) \sim T$  relation and calculating the values of  $a, b$  and  $E$

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$

$$= \frac{A_0}{\beta} \int_{T_0}^T T^a \exp\left(bT - \frac{dE}{R(T+c)}\right) \times$$

$$\left\{1 + (T - T_0) \left[\frac{a}{T} + \left[bT - \frac{dE}{R(T+c)^2}\right]\right]\right\} dT$$

$$= \frac{A_0}{\beta} T^a e^{bT} e^{-\frac{dE}{R(T+c)}} (T - T_0) \quad (35)$$

From the Eq. (55)

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} T^a \exp\left[bT - \frac{dE}{R(T+c)}\right] f(\alpha) \quad (55)$$

The following equations are obtained:

for the case of  $a = c = d = 0$ ,

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} e^{bT} f(\alpha) \quad (56)$$

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta} \int_0^T e^{bT} dT = \frac{A_0}{b\beta} e^{bT} \Big|_0^T = \frac{A_0}{b\beta} (e^{bT} - 1) \quad (57)$$

$$\ln \beta_i = \ln\left[\frac{A_0}{bG(\alpha)}\right] + bT_{ei} \quad i = 1, 2, \dots, L \quad (58)$$

for the case of  $b = c = d = 0$ ,

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} T^a f(\alpha) \quad (59)$$

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta} \int_0^T T^a dT = \frac{A_0}{\beta} \frac{1}{(a+1)} T^{a+1} \quad (60)$$

$$\ln \beta_i = \ln \left[ \frac{A_0}{(a+1)G(\alpha)} \right] + (a+1) \ln T_{ei} \quad (61)$$

$i = 1, 2, \dots, L$

for the case of  $a = b = c = 0$ , and  $d = 1$

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} e^{-E/RT} f(\alpha) \quad (62)$$

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta} \int_0^T e^{-E/RT} dT \quad (63)$$

$$\approx \frac{A_0 E}{\beta R} 0.00484 e^{-1.0516 \frac{E}{RT}}$$

$$\ln \beta_i = \ln \left[ \frac{A_0 E}{R G(\alpha)} \right] - 2.315 - 0.4567 \frac{E}{RT_{ei \text{ or } pi}} \quad (64)$$

$i = 1, 2, \dots, L$

The data ( $\beta_i$ ,  $T_{ei}$ ,  $T_{oi}$ ,  $i = 1, 2, \dots, L$ ) are filled to Eqs. (38), (40), (42), (58), (61) and (64) by the linear least-squares method on the computer. The corresponding values of  $a$ ,  $b$  and  $E$  may be obtained from the slopes of above-mentioned equations.

### 3 Experimental

#### 3.1 Materials

The seven furazano-fused cyclic compounds I-VII used in this work were prepared and purified at Xi'an Modern Chemistry Institute.

The structures of compounds I-VII were characterized by elemental analyses, molecular weight, IR spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry. Their purities were more than 99.0%. The compounds were kept in a vacuum desiccator before use.

#### 3.2 Experimental equipment and conditions

DSC experiments were carried out with a model CDR-1 thermal analyzer made in the Shanghai Balance Instrument Factory, using a Ni/Cr-Ni/Si thermocouple plate and working under static air conditions with different heating rates ranging from 0.5-20 K · min<sup>-1</sup>. Aluminum oxide was used as a reference material. Heating rate was calculated according to the actual rate of temperature rise from 50 °C to the temperature at the end of decomposition. The amount sample used was about 0.7 mg.

## 4 Results and discussion

The measured values of  $\beta_i$ ,  $T_{oi}$  and  $T_{ei}$  ( $i = 1, 2, \dots, L$ ), the calculated values of  $a$ ,  $b$  and  $E$  obtained by Eqs. (38), (40), (42), (58), (61) and (64) and the obtained values of  $T_{o0}$  and  $T_{e0}$  when  $\beta$  tends to zero, together with the reasonable values of  $T_b$  obtained by substituting the above-mentioned values into Eqs. (17), (18), (19), (26), (27), and (28), the values of  $E_k$  and  $\lg A_k$  obtained by the Kissinger's method<sup>[15]</sup>, and the entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) corresponding to  $T = T_{p0}$ ,  $A = A_k$ ,  $E = E_k$  obtained by Eqs. (65), (66) and (67) are shown in Table 1.

$$A e^{-\frac{E}{RT}} = \frac{k_b T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (65)$$

$$\Delta H^\ddagger = E - RT \quad (66)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (67)$$

Because the results of the six calculation formula are agreeable to each other, while the error between the values of  $T_b$  obtained by the determination method for the critical temperature of thermal explosion of small-scale solid explosive and the values of  $T_b$  from Eqs. (19) and (28) by non-isothermal DSC method is 5%<sup>[3]</sup>, we conclude that the values of  $T_b$  obtained by Eqs. (17)-(19) and Eqs. (26)-(28) also are tenable within the error of 5%, demonstrating that Eqs. (17), (18), (26) and (27) also are suitable for estimating the values of  $T_b$  of EMs.

## 5 Conclusion

(1) The eight calculation formulae of estimating the critical temperature of thermal explosion ( $T_b$ ) of EMs are derived.

(2) The corresponding numerical methods for estimating the values of  $T_b$  are presented.

(3) The values of  $T_b$  of compounds I-VII decrease in the order II > IV > III > VII > V > VI > I.

(4) The heat-resistance ability of compounds I-VII determined by values of  $\Delta G^\ddagger$  based on the greater the values of  $\Delta G^\ddagger$ , the better the stability of samples decreases in the order II ≈ IV > III > VII > V ≈ VI > I.

Table 1 The calculated values of the critical temperature of thermal explosion and thermodynamic parameters of activation reaction for seven furazano – fused cyclic compounds

sample No.	$\beta$ /K · min <sup>-1</sup>	$T_0$ /K	$T_e$ /K	$T_p$ /K	$T_{00}$ /K	$T_{40}$ /K	$T_{60}$ /K	Eq. (38)		Eq. (40)		Eq. (42)		Eq. (58)		Eq. (61)		Eq. (62)		$T_b$ /K	$E_k$ /kJ · mol <sup>-1</sup>	$\lg(A_0/s^{-1})$ /kJ · mol <sup>-1</sup>	$\Delta G^\ddagger$ /kJ · mol <sup>-1</sup>	$\Delta H^\ddagger$ /kJ · mol <sup>-1</sup>	$\Delta S^\ddagger$ /J · mol <sup>-1</sup> · K <sup>-1</sup>
								$b$	$a$	$b$	$a$	$b$	$a$	$b$	$a$	$b$	$a$	$b$	$a$						
I	2.125	342.08	348.83	361.68	335.98	342.56	355.29	0.0724	26.37	79.85	0.0737	25.85	81.67 <sup>1)</sup>	352.00	351.85	351.49 <sup>1)</sup>	355.65	356.35	355.92 <sup>5)</sup>	79.61	8.91	106.54	76.66	-84.11	
	5.00	353.15	359.80	372.90									(77.3) <sup>2)</sup>		(351.99) <sup>4)</sup>			(356.78) <sup>6)</sup>							
	10.60	363.02	370.02	383.27																					
II	21.85	373.52	380.47	393.82																					
	2.135	458.61	480.46	492.96	455.33	477.08	488.85	0.0896	44.16	180.95	0.0901	43.45	184.5	485.89	485.90	485.75	487.94	488.32	488.05	185.6	17.15	146.84	181.54	70.98	
	5.00	471.15	493.15	505.15									(173.1)		(488.28)			(488.83)							
III	10.75	475.24	497.39	510.64																					
	22.15	484.85	507.00	518.95																					
	2.222	451.65	462.50	472.15	447.17	458.19	467.56	0.1299	61.20	239.76	0.1291	59.85	231.9	464.05	464.03	464.18	465.81	465.98	466.11	235.9	23.77	139.40	232.01	198.08	
IV	5.571	458.65	469.20	479.15									(226.7)		(464.31)			(466.30)							
	10.50	464.45	474.90	485.15																					
	22.89	469.55	480.30	490.15																					
V	1.040	427.30	471.65	485.90	422.58	465.38	479.73	0.0759	37.27	151.95	0.0756	36.09	156.3	476.39	476.30	475.92	478.26	478.64	477.83	155.9	13.94	147.26	151.91	9.68	
	2.085	435.40	478.90	492.40									(143.8)		(476.80)			(479.01)							
	5.290	445.65	491.00	504.40																					
VI	10.32	458.70	501.55	514.40																					
	20.55	466.30	510.25	523.40																					
	0.8659	393.50	409.00	412.15	391.17	406.54	409.83	0.1868	77.99	270.68	0.1888	77.86	263.9	410.95	410.93	411.01	411.77	411.83	411.96	270.5	31.76	122.78	267.09	352.13	
VII	2.000	396.85	412.70	415.65									(260.3)		(411.06)			(412.03)							
	5.037	401.72	417.79	420.65																					
	10.83	405.65	421.90	425.15																					
VIII	22.71	410.15	426.15	429.15																					
	1.032	381.00	401.15	412.65	377.85	398.37	409.96	0.1503	61.88	211.79	0.1493	60.50	214.0	403.90	403.87	403.78	404.96	405.06	404.84	218.1	25.09	122.68	214.69	224.44	
	2.136	385.35	405.30	416.15									(200.1)		(404.13)			(405.31)							
IX	5.306	390.50	410.15	421.15																					
	11.04	394.75	415.00	426.15																					
	21.07	402.15	421.70	432.65																					
X	1.102	400.85	416.30	428.15	398.10	413.81	425.62	0.1886	80.05	282.49	0.1889	79.20	275.4	418.20	418.18	418.26	419.04	419.10	419.18	282.4	32.03	126.92	278.86	356.99	
	2.146	403.00	419.00	431.15									(269.1)		(418.35)			(419.31)							
	5.083	407.76	423.15	435.15																					
XI	10.87	411.95	427.40	439.15																					
	23.88	416.65	432.50	445.15																					

Note: 1) Values of E calculated from the relationship of  $\ln \beta_1$  vs.  $1/T_{pi}$ ; 2) The data in parentheses are obtained by Eq. (64) from the relationship of  $\ln \beta_1$  vs.  $1/T_{er}$ ; 3) The value of  $T_b$  obtained using the data of  $T_{00}$ ,  $T_{e0}$  and E from Eq. (42); 4) The data in parentheses are obtained by Eq. (19) using the data of  $T_{00}$ ,  $T_{e0}$  and E obtained from the relationship of  $\ln \beta_1$  vs.  $1/T_{er}$ ; 5) The value of  $T_b$  obtained by the data of  $T_{e0}$  and E obtained from the relationship of  $\ln \beta_1$  vs.  $1/T_{pi}$ ; 6) The data in parentheses are obtained using the data of  $T_{e0}$  and E obtained from the relationship of  $\ln \beta_1$  vs.  $1/T_{er}$ .

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## 用非等温 DSC 估算一些呋咱环化合物的热爆炸临界温度

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**摘要:** 通过合理假设, 从谢苗诺夫 (Semenov) 热爆炸理论和 8 个非等温动力学方程, 导出了估算含能材料 (EMs) 热爆炸临界温度 ( $T_b$ ) 的 2 个通式和它们的 6 个派生式。从 EMs 的非等温 DSC 曲线可获得 DSC 曲线偏离基线的起始温度 ( $T_0$ )、onset 温度 ( $T_{oi}$ ) 和放热分解反应的动力学参数。由方程  $T_{oi \text{ or } ei} = T_{00 \text{ or } e0} + a_1\beta_i + a_2\beta_i^2 + \dots + a_{L-2}\beta_i^{L-2}$ ,  $i = 1, 2, \dots, L$  可得到  $T_{00}$  和  $T_{e0}$  值, 随后用 6 个派生式可计算  $T_b$  值。对 1,4,5,8-四硝基-1,4,5,8-四氮杂双呋咱 [3,4-c:3',4'-h] 十氢化萘, 1,4,5,8-四氮杂双呋咱 [3,4-c:3',4'-h] 十氢化萘, 1,3,4-三硝基咪唑烷酮 [4,5-b] 呋咱 [3,4-e] 哌嗪, 咪唑烷酮 [4,5-b] 呋咱 [3,4-e] 哌嗪, 1,3,4,8-四硝基咪唑烷酮 [4,5-b] 呋咱 [3,4-e] 哌嗪, 1,4,5,8-四硝基-1,4,5,8-四氮杂萘呋咱 [3,4-b] 十氢化萘, 1,3,5-三硝基-1,3,5-三氮杂呋咱 [3,4-f] 环庚烷, 由 6 个派生式所得的  $T_b$  值甚接近。

**关键词:** 物理化学; 呋咱环化合物; 临界温度; 热爆炸; 非等温 DSC

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