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Theory and Numerical Method of Calculating the Kinetic Parameters of Exothermic Decomposition Reaction of Energetic Materials from Peak Temperature of DSC Curves at Constant Heating Rates

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Abstract: Two mathematical expressions for calculating the kinetic parameters of exothermic decomposition reaction of energetic materials (EMs) are derived from peak temperature of DSC curves at constant heating rates based on Kooij's formula and van't Hoff's formula, the corresponding numerical method for calculating the kinetic parameters are presented. The E results obtained with the two derived formulae and Kissinger's method, Ozawa's method, Tang's method, Hu-Gao-Zhang method and integral isoconversional non-linear method (NL-INT) for 2,4,6-trinitro-2,4,6-triazacyclohexanone (Keto-RDX), approximate well to each other, showing that taking the value of a of 0.5 and the value of b of 0.003 are suitable for calculating the kinetic parameters by the two derived formulae.

Key words: physical chemistry; DSC; kinetic parameter; Kooij's formula; van't Hoff Formula; Keto-RDX; non-isothermal

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1 Introduction

The apparent activation energy (E) and pre-exponential constant (A) are two important parameters from the point of view of evaluation of stability, safety and compatibility for energetic materials (EMs). Much research based on Arrhenius formula, $k = Ae^{\frac{-E}{RT}}$ (where E and A are constant) has already been done in this area[1]. Seldom, however, have the studies on the values of E_{KJ}, $A_{0,KJ}$, E_{vH} and $A_{0,vH}$ based on Kooij's formula, $k = A_{0,KJ}T^{a}\exp\left(\frac{-E_{KJ}}{RT}\right)$ and van't Hoff's formula $k = A_{0,vH}\exp(bT)\exp\left(\frac{-E_{vH}}{RT}\right)$ (where A in $A = A_{0,KJ}T^{a}$ and $A = A_{0,vH}\exp(bT)$ is not strictly constant) been reported. In this work, we report the theory and numerical method of calculating the kinetic parameters of exothermic decomposition reaction of EMs from peak temperature of DSC curves at constant heating rates based on Kooij's formula and van't Hoff's formula and calculate values of E_{KJ}, E_{vH}, $A_{0,KJ}$ and $A_{0,vH}$ for the thermal decomposition reaction of Keto-RDX.

2 Theory and method of calculating the kinetic parameters based on Kooij's formula

The basic isothermal differential rate equation describing the change of the conversion degree with time based on Kooij's formula[1]3 is

$$\frac{d\alpha}{dt} = k[1-\alpha(t)]^{n} = A_{0}T^{a}\exp\left(-\frac{E}{RT}\right)[1-\alpha(t)]^{n} \quad (1)$$

where α is the decomposition extent; t is time in s; A_0 is the factor, a is any constant in the range of 0.5 to 4.0 with the step size of 0.5, for thermal decomposition reaction of EMs, usually the value of a takes 0.5; E, T and R are the apparent activation energy in J·mol^{-1}, the temperature in K, and the gas constant in 8.314 J·mol^{-1}·K^{-1}, respectively.

It is believed that Eq. (1) is also valid for non-

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isothermal cases (at least empirically).

Setting T_0 as the initial temperature at which the peak on the DSC or DTG curve deviates from its baseline in K, β as the constant heating rate in $\mathrm{K \cdot s^{-1}}$, t as heating time in s and T as the reaction temperature at time t in K, we have

$$T = T_0 + \beta t \tag{2}$$

In order to obtain an overall relationship for non-isothermal kinetics, Eqs. (1) and (2) are combined to yield

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A_0}{\beta} T^a \exp\left(-\frac{E}{RT}\right)[1-\alpha(T)]^n \tag{3}$$

If the temperature rises at a constant heating rate β, and the kinetic parameters at any conversion degree are approximately equal to those of its neighboring conversion degree, then by differentiation of Eq. (3) with respect to T,

$$\begin{aligned}
\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} &= \frac{\mathrm{d}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)}{\mathrm{d}T} = \frac{\mathrm{d}\left(\frac{A_0}{\beta}T^a \mathrm{e}^{-E/RT} \cdot (1-\alpha(T))^n\right)}{\mathrm{d}T} \\
&= \left[\frac{A_0}{\beta} a T^{a-1} \mathrm{e}^{-E/RT} + \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT} \cdot \left(\frac{E}{RT^2}\right)\right] \cdot (1-\alpha(T))^n + \\
&\quad \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT} [n(1-\alpha(T))^{n-1}] \cdot \left(-\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) \\
&= \left[\frac{A_0}{\beta} a T^{a-1} \mathrm{e}^{-E/RT} + \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT} \cdot \left(\frac{E}{RT^2}\right)\right] \cdot (1-\alpha(T))^n - \\
&\quad \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT} [n(1-\alpha(T))^{n-1}] \cdot \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT} (1-\alpha(T))^n \\
&= \frac{1}{\beta}[A_0 T^a \mathrm{e}^{-E/RT} (1-\alpha(T))^n] \cdot \\
&\quad \left[\frac{a}{T} + \frac{E}{RT^2} - n(1-\alpha(T))^{n-1} \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT}\right] \\
&= \frac{1}{\beta}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\left[\frac{a}{T} + \frac{E}{RT^2} - n(1-\alpha(T))^{n-1} \frac{A_0}{\beta} T^a \mathrm{e}^{-E/RT}\right] \\
&= \frac{1}{\beta}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\left[\frac{a}{T} + \frac{E}{RT^2} + n(1-\alpha(T))^{-1}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\right]
\end{aligned} \tag{4}$$

Rearranging both sides of Eqs. (3) and (4) gives the following expressions for n and E

$$\begin{aligned}
E &= -RT\ln\left[\frac{\beta \frac{\mathrm{d}\alpha}{\mathrm{d}T}}{A_0 T^a [1-\alpha(T)]^n}\right] \overset{\beta = \frac{\mathrm{d}T}{\mathrm{d}t}}{=} -RT\ln\left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{A_0 T^a [1-\alpha(T)]^n}\right] \\
&\overset{a=\frac{1}{2}}{=} -RT\ln\left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{A_0 T^{0.5} [1-\alpha(T)]^n}\right]
\end{aligned} \tag{5}$$

$$\begin{aligned}
n &= \frac{\left[\beta\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\right) / \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) - \frac{E}{RT^2} - \frac{a}{T}\right](1-\alpha(T))}{\left(-\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)} \\
&\overset{a=\frac{1}{2}}{=} \frac{\left[\beta\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\right) / \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) - \frac{E}{RT^2} - \frac{1}{2}T^{-1}\right](1-\alpha(T))}{\left(-\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)}
\end{aligned} \tag{6}$$

When

$$\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\right)_{T=T_\mathrm{p},\, \alpha=\alpha_\mathrm{p}} = 0 \tag{7}$$

occurs the maximum reaction rate.

Therefore, Eq. (4) at maximum rate gives

$$\frac{a}{T_\mathrm{p}} + \frac{E}{RT_\mathrm{p}^2} = n(1-\alpha_\mathrm{p})^{n-1} \frac{A_0}{\beta} T_\mathrm{p}^a \mathrm{e}^{-E/RT_\mathrm{p}} \tag{8}$$

and

$$\begin{aligned}
\beta &= \frac{n(1-\alpha_\mathrm{p})^{n-1} A_0 T_\mathrm{p}^a \mathrm{e}^{-E/RT_\mathrm{p}}}{\frac{a}{T_\mathrm{p}} + \frac{E}{RT_\mathrm{p}^2}} = \frac{n(1-\alpha_\mathrm{p})^{n-1} A_0 T_\mathrm{p}^a \mathrm{e}^{-E/RT_\mathrm{p}}}{\frac{1}{T_\mathrm{p}}\left(a + \frac{E}{RT_\mathrm{p}}\right)} \\
&= \frac{n(1-\alpha_\mathrm{p})^{n-1} A_0 T_\mathrm{p}^{a+1} \mathrm{e}^{-E/RT_\mathrm{p}}}{a + \frac{E}{RT_\mathrm{p}}}
\end{aligned} \tag{9}$$

where T_p and α_p are the peak temperature of DSC or DTG curve and decomposition extent at peak temperature, respectively.

By taking the natural logarithm on both sides of the Eq. (9), one obtains

$$\begin{aligned}
\ln\beta &= \ln n + (n-1)\ln(1-\alpha_\mathrm{p}) + \ln A_0 + \\
&\quad (a+1)\ln T_\mathrm{p} - \frac{E}{RT_\mathrm{p}} - \ln\left(a + \frac{E}{RT_\mathrm{p}}\right)
\end{aligned} \tag{10}$$

Substituting the values of $n = 1$ into Eq. (10), gives the following equation

$$\ln\beta = \ln A_0 + (a+1)\ln T_\mathrm{p} - \ln\left(\frac{E}{RT_\mathrm{p}} + a\right) - \frac{E}{RT_\mathrm{p}} \tag{11}$$

The plot of $\ln\beta$ versus $\frac{1}{T_\mathrm{p}}$ should give a straight line with the slope $-\frac{E}{R}$ giving the activation energy E at maximum rate, and A_0 can be calculated from the activation energy E and the intercept $\ln A_0 + (a+1)\ln T_\mathrm{p} - \ln\left(\frac{E}{RT_\mathrm{p}} + a\right)$.

On rearrangement on both sides of the Eq. (11), the following equation is obtained

$$\ln\left[\frac{\beta_i\left(a + \frac{E}{RT_{\mathrm{p}i}}\right)}{T_{\mathrm{p}i}^{a+1}}\right] = \ln A_0 - \frac{E}{RT_{\mathrm{p}i}} \tag{12}$$

Equation (12) may be solved by the iterative method on the computer when the value of a is supposed. Any arbitrary value may be assumed for E ($E > 0$), and using this value and original data (β_i, $T_{\mathrm{p}i}$ $i = 1, 2, \cdots, L$), the value of the expression on the left-hand side may be calculated for each data point. This, when plotted against $(1/T)$ by the linear least-squares method, gives new values of E from the slope and A_0 from the intercept. This modified value of E is used as a starting value for the next iteration which yields another modified value of E. Thus after a few iterations, consistent values of E and A_0 will be obtained.

Using Frank-Kameneskii's expression [1]31

$$\int_0^T \mathrm{e}^{-E/RT}\mathrm{d}T = \frac{RT^2}{E}\mathrm{e}^{-E/RT} \qquad (13)$$

Integrating of Eq. (3) for the temperature between 0 and T, and the decomposition extent between 0 and α results in

$$\begin{aligned} G(\alpha) &= \int_0^\alpha \frac{\mathrm{d}\alpha}{[1-\alpha(T)]^n} = \frac{A_0}{\beta}\int_0^T T^a \mathrm{e}^{-E/RT}\mathrm{d}T = \frac{A_0 R}{\beta E}\int_0^T T^{a+2}\mathrm{d}\mathrm{e}^{-E/RT} \\ &= \frac{A_0 R}{\beta E}\left(T^{a+2}\mathrm{e}^{-E/RT}\Big|_0^T - (a+2)\frac{R}{E}\int_0^T T^{a+1}\mathrm{e}^{-E/RT}\mathrm{d}T\right) \\ &= \frac{A_0 R}{\beta E}\left((T^{a+2}\mathrm{e}^{-E/RT} - 0) - (a+2)\frac{R}{E}\int_0^T T^{a+3}\mathrm{d}\mathrm{e}^{-E/RT}\right) \\ &= \frac{A_0 R}{\beta E}\left(T^{a+2}\mathrm{e}^{-E/RT} - (a+2)\frac{R}{E}\left(T^{a+3}\mathrm{e}^{-E/RT}\Big|_0^T - \int_0^T T^{a+4}\mathrm{d}\mathrm{e}^{-E/RT}\right)\right) \\ &\approx \frac{A_0 R}{\beta E}\left(T^{a+2}\mathrm{e}^{-E/RT} - (a+2)\frac{R}{E}(T^{a+3}\mathrm{e}^{-E/RT} - 0)\right) \\ &= \frac{A_0 R}{\beta E}T^{a+2}\mathrm{e}^{-E/RT}\left(1-(a+2)\frac{R}{E}T\right) \\ &\overset{a=\frac{1}{2}}{=} \frac{A_0 R}{\beta E}T^{\frac{5}{2}}\mathrm{e}^{-E/RT}\left(1-\frac{5}{2}\frac{R}{E}T\right) \qquad (14) \end{aligned}$$

Taking logarithm on both sides of equation (14), the integral equation (15) may be obtained

$$\ln\left[\frac{G(\alpha)}{T^{a+2}\left(1-(a+2)\dfrac{RT}{E}\right)}\right] \overset{a=\frac{1}{2}}{=} \ln\left[\frac{G(\alpha)}{T^{\frac{5}{2}}\left(1-\dfrac{5}{2}\dfrac{RT}{E}\right)}\right] = \ln\left(\frac{A_0 R}{\beta E}\right) - \frac{E}{RT} \qquad (15)$$

For getting the values of E and A, the data (β, T_i, α_i, $i=1, 2, \cdots, L$) are fitted to Eq. (15) by the linear least-squares method in a similar way to solve the Eq. (12) on the computer.

2.1 Relation of E and E_0

The relationship between the kinetic constant (k) and the absolute temperature (T) of reaction is expressed by Arrhenius equation

$$k = A\exp(-E/RT) \qquad (16)$$

where E and A are the activation energy and pre-exponential constant, respectively; R is the gas constant.

Taking natural logarithm on both sides of the Eq. (16), Eq. (17) is obtained

$$\ln k = \ln A - \frac{E}{RT} \qquad (17)$$

On differentiation, rearrangement on both sides of the Eq. (17), Eqs. (18) and (19) are obtained

$$\mathrm{d}\ln k = \frac{E}{RT^2}\mathrm{d}T \qquad (18)$$

$$E = RT^2\frac{\mathrm{d}\ln k}{\mathrm{d}T} \qquad (19)$$

Similarly, the following equations can be obtained if $k = A_0 T^a \exp(-E_0/RT)$

$$\ln k = \ln A_0 + \ln T^a - \frac{E_0}{RT} \qquad (20)$$

$$\begin{aligned} \mathrm{d}\ln k &= 0 + \frac{\mathrm{d}T^a}{T^a} + \frac{E_0}{RT^2}\mathrm{d}T \\ &= \frac{aT^{a-1}\mathrm{d}T}{T^a} + \frac{E_0}{RT^2}\mathrm{d}T \\ &= \frac{a}{T}\mathrm{d}T + \frac{E_0}{RT^2}\mathrm{d}T \qquad (21) \end{aligned}$$

$$E_0 + aRT = \frac{\mathrm{d}\ln k}{\mathrm{d}T} \qquad (22)$$

Combining Eqs. (19) and (22), we obtain

$$E = E_0 + aRT \qquad (23)$$

Equation (23) is the relation formula between the E and E_0.

3 Theory and method of calculating the kinetic parameters based on van't Hoff's formula

The basic isothermal differential rate equation describing the change of the decomposition extent with time based on van't Hoff's formula[1]3 is

$$\begin{aligned} \frac{\mathrm{d}\alpha}{\mathrm{d}t} &= k[1-\alpha(t)]^n \\ &= A_0\exp(bT)\exp\left(-\frac{E}{RT}\right)[1-\alpha(t)]^n \qquad (24) \end{aligned}$$

where b is any constant in the range of 0.0001 to 0.01, for thermal decomposition reaction of EMs, usually the value of b takes 0.003.

It is believed that Eq. (24) is also valid for non-isothermal cases (at least empirically).

In order to obtain an overall relationship for non-isothermal kinetics, Eqs. (24) and (2) are combined to yield

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A_0}{\beta}\mathrm{e}^{bT}\exp\left(-\frac{E}{RT}\right)[1-\alpha(T)]^n \qquad (25)$$

If the temperature rises at a constant heating rate β, and the kinetic parameters at any decomposition extent are approximately equal to those of its neighboring decomposition extent, then by differentiation of Eq. (26) with respect to T,

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} = \frac{\mathrm{d}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)}{\mathrm{d}T} = \frac{\mathrm{d}\left(\frac{A_0}{\beta}\mathrm{e}^{bT}\mathrm{e}^{-E/RT}\cdot f(\alpha)\right)}{\mathrm{d}T}$$

$$= \frac{A_0}{\beta}\Big[b\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f(\alpha) + \mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot\left(\frac{E}{RT^2}\right)\cdot f(\alpha) +$$

$$\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f'(\alpha)\cdot\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\Big]$$

$$= \frac{A_0}{\beta}\Big[b\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f(\alpha) + \mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot\left(\frac{E}{RT^2}\right)\cdot f(\alpha) +$$

$$\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f'(\alpha)\cdot\frac{A_0}{\beta}\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f(\alpha)\Big]$$

$$=\frac{A_0}{\beta}\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f(\alpha)\left[b+\left(\frac{E}{RT^2}\right)+\frac{A_0}{\beta}\mathrm{e}^{bT}\cdot\mathrm{e}^{-E/RT}\cdot f'(\alpha)\right] \tag{26}$$

When $$\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\right)_{T=T_\mathrm{p},\alpha=\alpha_\mathrm{p}} = 0 \tag{27}$$

occurs the maximum reaction rate.

The nth order reaction equation $f(\alpha) = (1-\alpha)^n$, $f'(\alpha) = (-1)n(1-\alpha)^{n-1}$. Therefore, Eq. (26) at maximum rate gives

$$b + \frac{E}{RT_\mathrm{p}^2} = n(1-\alpha_\mathrm{p})^{n-1}\frac{A_0}{B}\mathrm{e}^{bT_\mathrm{p}}\cdot\mathrm{e}^{-E/RT_\mathrm{p}} \tag{28}$$

and

$$\beta = \frac{n(1-\alpha_\mathrm{p})^{n-1}A_0\mathrm{e}^{bT_\mathrm{p}}\cdot\mathrm{e}^{-E/RT_\mathrm{p}}}{b+\frac{E}{RT_\mathrm{p}^2}} \tag{29}$$

where T_p and α_p are the peak temperature of DSC or DTG curve and decomposition extent at peak temperature, respectively.

By taking the natural logarithm on both sides of the Eq. (29), one obtains

$$\ln\beta = \ln n(1-\alpha_\mathrm{p})^{n-1} + \ln A_0 +$$

$$bT_\mathrm{p} - \frac{E}{RT_\mathrm{p}} - \ln\left(b + \frac{E}{RT_\mathrm{p}^2}\right) \tag{30}$$

Integrating of Eq. (25) for the temperature between 0 and T, and the decomposition extent between 0 and α, results in

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A_0}{\beta}\int_0^T\mathrm{e}^{bT}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{31}$$

$$u = \frac{E}{RT} \tag{32}$$

$$\int_0^T\mathrm{e}^{bT}\cdot\exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \left(-\frac{E}{R}\right)\int_\infty^u\frac{1}{u^2}\exp\left(\frac{bE}{Ru}-u\right)\mathrm{d}u$$

$$= \left(-\frac{E}{R}\right)\int_\infty^u\frac{-R}{bE+Ru^2}\mathrm{d}\mathrm{e}^{\left(\frac{bE}{Ru}-u\right)}$$

$$= \frac{E}{bE+Ru^2}\mathrm{e}^{\left(\frac{bE}{Ru}-u\right)} - \frac{2R^2Eu^3}{(bE+Ru^2)^3}\mathrm{e}^{\left(\frac{bE}{Ru}-u\right)} -$$

$$\frac{6ER^3u^4(bE-Ru^2)}{(bE+Ru^2)^5}\mathrm{e}^{\left(\frac{bE}{Ru}-u\right)} + 6ER^3\int_\infty^u\mathrm{e}^{\left(\frac{bE}{Ru}-u\right)}\mathrm{d}\left[\frac{u^4(bE-Ru^2)}{(bE+Ru^2)^5}\right]$$

$$\approx \frac{E}{bE+Ru^2}\mathrm{e}^{\left(\frac{bE}{Ru}-u\right)}\left[1-\frac{2R^2Eu^3}{(bE+Ru^2)^2}\right]$$

$$\overset{u=\frac{E}{RT}}{=} \frac{RT^2}{bRT^2+E}\mathrm{e}^{\left(bT-\frac{E}{RT}\right)}\left[1-\frac{\frac{2E}{T^3}}{\left(b+\frac{E}{RT^2}\right)^2}\right] \tag{33}$$

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A_0}{\beta}\frac{RT^2}{bRT^2+E}\mathrm{e}^{\left(bT-\frac{E}{RT}\right)}\left[1-\frac{\frac{2E}{T^3}}{\left(b+\frac{E}{RT^2}\right)^2}\right] \tag{34}$$

$$n\neq 1,\ \frac{1}{n-1}\left[\frac{1}{(1-\alpha)^{n-1}}-1\right] =$$

$$\frac{A_0}{\beta}\frac{RT^2}{bRT^2+E}\left[1-\frac{2R^2TE}{(bRT^2+E)^2}\right]\mathrm{e}^{\left(bT-\frac{E}{RT}\right)} \tag{35}$$

Eq. (28) becomes

$$n(1-\alpha)^{n-1} = \frac{b+\frac{E}{RT_\mathrm{p}^2}}{\frac{A_0}{\beta}\mathrm{e}^{bT_\mathrm{p}-\frac{E}{RT_\mathrm{p}}}} \tag{36}$$

Combining Eqs. (35) and (36), $T = T_\mathrm{p}$, yields

$$\frac{n}{n-1}\left[1-(1-\alpha_\mathrm{p})^{n-1}\right] = \left[1-\frac{2R^2TE}{(bRT^2+E)^2}\right] \tag{37}$$

When $\frac{2R^2TE}{(bRT^2+E)^2}\ll 1$, yields

$$\frac{n}{n-1}\left[1-(1-\alpha_\mathrm{p})^{n-1}\right]\approx 1 \tag{38}$$

$$n(1-\alpha_\mathrm{p})^{n-1} = 1 \tag{39}$$

Combining Eqs. (30) and (39), yields

$$\ln\beta + \ln\left(b+\frac{E}{RT_\mathrm{p}^2}\right) - bT_\mathrm{p} = \ln A_0 - \frac{E}{RT_\mathrm{p}} \tag{40}$$

On rearrangement on both sides of the Eq. (40), the following equation is obtained

$$\ln\left[\frac{\beta_i\left(b+\frac{E}{RT_{\mathrm{p}i}}\right)}{\mathrm{e}^{bT_{\mathrm{p}i}}}\right] = \ln A_0 - \frac{E}{RT_{\mathrm{p}i}} \tag{41}$$

Equation (41) may be solved by the iterative method on the computer. Any arbitrary value may be assumed for $E(E>0)$, and using this value and original data (β_i,

$T_{pi}, i = 1, 2, \cdots, L$), the value of the expression on the left-hand side may be calculated for each data point. This, when plotted against ($1/T_{pi}$) by the linear least-squares method, gives new values of E from the slope and A_0 from the intercept. This modified value of E is used as a starting value for the next iteration which yields another modified value of E. Thus after a few iterations, consistent values of E and A_0 will be obtained.

4 Experimental

Keto-RDX used in this work was prepared and purified by the Modern Chemistry Institute, Lanzhou, Gansu, China. The sample was kept in a vacuum desiccator before use.

DSC experiments of Keto-RDX were carried out with a model CDR thermal analyzer made in the Shanghai Balance Instrument Factory, using a Ni/Cr-Ni/Si thermocouple plate and working in static air with heating rates 0.5 – 22 K · min^{-1}. α-Al_2O_3 was used as the reference material. The DSC curves were obtained with a cell of aluminum (5 mm × 3 mm), the side of which was rolled up. The heating rate was calculated according to the actual rate of temperature rise from 50 ℃ to the temperature at the end of the decomposition. The amount of sample used was about 0.7 mg. DSC curves obtained under the same conditions overlap each other, indicating that the reproducibility of tests was satisfactory.

5 Results and discussion

5.1 The thermal decomposition behavior of Keto-RDX under static air conditions

A typical DSC curve at a heating rate of 22.73 K · min^{-1} is shown in Fig. 1. From Fig. 1 it can be seen that Keto-RDX decomposes partly before melting, and the melting is accompanied by decomposition.

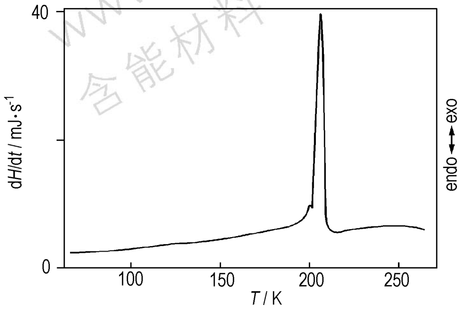

Fig. 1 DSC curve of the thermal decomposition of Keto-RDX at a heating rate of 22.73 K · min^{-1}

The endothermic peak at 195 ℃ is the phase change from solid to liquid. The exothermic peak at 208 ℃ is caused by the rapid decomposition reaction in molten state.

5.2 Analysis of kinetic data

In order to obtain the kinetic parameters (the apparent activation energy E and pre-exponential constant A) of the major exothermic decomposition reaction of Keto-RDX, the seven multiple heating methods in Tables 1 and Table 2 are employed. Form the original data in Table 1, the values of E_K and A_K obtained by Kissinger's method[1]79 and the values of E_O, E_T, E_{HGZ}, $E_{NL\text{-}INT}$ obtained by Ozawa's method[1]57, Tang's method[1]74, Hu-Gao-Zhang method[1]73 and integral isoconversional non-linear method[1]236 in Table 1, and the values of E_{Kj} and E_{vH} obtained by Eqs. (12) and (41) based on Kooij's formula and van't-Hoff formula in Table 2 are obtained, indicating that the values of E_{Kj} and E_{vH} obtained from Eqs. (12) and (41) when the values of a and b in Eqs. (12) and (41) take 0.5 and 0.003, respectively approach to the values of E_K, E_O, E_T, E_{HGZ} and $E_{NL\text{-}INT}$ in Table 1. This may be the reason why the value of a in Eq. (12) takes 0.5 for calculating the value of E from Eq. (12) and the value of b in Eq. (41) takes 0.003 for calculating the value of E from Eq. (41).

The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \to 0$ by Eq. (42) taken from[1]307 using the data of T_p and β in Table 1 is 439.56 K

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3 + e\beta_i^4 \quad i = 1, 2, \cdots, 6 \quad (42)$$

The values of the critical temperature of thermal decomposition (T_b) obtained from Eq. (43) taken from[1]307 using the values of T_{po} and E_O in Table 1, and E_{Kj} corresponding to $a = 0.5$ and E_{vH} corresponding to $b = 0.003$ in Table 2 are 448.71, 448.68 and 448.66 K, respectively.

$$T_b = \frac{E_{O\text{ or }Kj\text{ or }vH} - \sqrt{E_{O\text{ or }Kj\text{ or }vH}^2 - 4E_{O\text{ or }Kj\text{ or }vH}RT_{p0}}}{2R} \quad (43)$$

where R is the gas constant (8.314 J · mol^{-1} · K^{-1}) and $E_{O\text{ or }Kj\text{ or }vH}$ is apparent activation energy obtained by Ozawa's method or Eq. (12), or Eq. (41).

The lg$A$ versus E relationship can be described by mathematic expression for the kinetic compensation effect, $\lg A = a_1 E + b_1$, for Keto-RDX

$$\lg A_{0,KJ} = 0.8197E_{KJ} - 133.344 \quad r_{KJ} = 1.0$$

$$\lg A_{0,vH} = 0.2282E_{vH} - 21.436 \quad r_{vH} = 1.0.$$

Table 1 Kinetic parameters of thermal decomposition of Keto-RDX under static atmosphere calculated by Kissinger's method, Ozawa's method, Tang's method, Hu-Gao-Zhang method and NL-INT method 1)

β /K · min^{-1}	T_p/K	E_K /kJ · mol^{-1}	lg(A_K/s^{-1})	E_O /kJ · mol^{-1}	E_T /kJ · mol^{-1}	E_{HGZ} /kJ · mol^{-1}	$E_{NL\text{-}NIT}$ /kJ · mol^{-1}	T_{p0}/K	T_b/K
0.5172	446.15	184.69	18.55	182.95	184.82	185.41	184.82	439.56	448.71
1.008	453.15								
2.162	461.15								
5.385	470.15								
10.47	474.15								
22.73	481.15								

Note: 1) β, heating rate; T_p, maximum peak temperature; E, apparent activation energy; A, pre-exponential constant; subscript K, data obtained by Kissinger's method; subscript O, data obtained by Ozawa's method; subscript T, data obtained by Tang's method; subscript HGZ, data obtained by Hu-Gao-Zhang method; subscript NL-INT, data obtained by integral isoconversional non-linear method; T_{p0}, the value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \to 0$ by Eq. (42); T_b, data obtained from Eq. (43) using the data of E_o and T_{p0}.

Table 2 Kinetic parameters of thermal decomposition of Keto-RDX under static air conditions calculated by Eqs. (12) and (41)

Eq. (12)			Eq. (41)		
a	E_{KJ} /kJ · mol^{-1}	lg($A_{0,KJ}$/s^{-1})	b	E_{vH} /kJ · mol^{-1}	lg($A_{0,vH}$/s^{-1})
0	185.41	18.64	0	189.26	21.74
0.5	183.53	17.09	0.001	187.48	21.34
0.6	183.15	16.78	0.002	185.70	20.93
0.7	182.77	16.47	0.003	183.91	20.53
1.0	181.64	15.55	0.004	182.13	20.12
1.5	179.76	14.00	0.005	180.35	19.71
2.0	177.87	12.46	0.006	178.56	19.31
2.5	175.99	10.91	0.007	176.78	18.90
3.0	174.10	9.36	0.008	175.00	18.49
3.5	172.22	7.82	0.009	173.21	18.09
4.0	170.33	6.27	0.010	171.43	17.68
4.5	168.45	4.73	0.011	169.65	17.27
5.0	166.56	3.18	0.012	167.86	16.87
5.5	164.68	1.64	0.013	166.08	16.46
6.0	162.79	0.09	0.014	164.30	16.05
6.5	160.91	-1.45	0.015	162.51	15.64
7.0	159.02	-3.00	0.016	160.73	15.24
7.5	157.14	-4.54	0.017	158.95	14.83
			0.018	157.16	14.42
			0.019	155.38	14.01
			0.020	153.60	13.61

6 Conclusions

(1) The two formulae of calculating the kinetic parameters of exothermic decomposition reaction of EMs are derived from peak temperature (T_p) of DSC curves at different constant heating rates (β) based on Kooij's equation and van't Hoff's equation.

(2) The corresponding numerical methods for calculating the values of E_{KJ}, $A_{0,KJ}$, E_{vH} and $A_{0,vH}$ are presented.

(3) With the help of data, β_i, T_{pi}, $i = 1, 2, \cdots, 6$, the values of E_{KJ} and E_{vH} obtained from Eqs (12) and (41) based on Kooij's equation and van't Hoff's equation when the values of a and b take 0.5 and 0.003 respectively, which approach to the values of E_K, E_O, E_{HGZ} and $E_{NL\text{-}INT}$ obtained from Kissinger's equation, Ozawa's equation, Tang's equation, Hu-Gao-Zhang equation and the integral isoconversional non-linear equation based on Arrhenius formula.

(4) For the thermal decomposition reaction of Keto-RDX, when $a = 0.5$, $E_{KJ} = 183.53$ kJ · mol^{-1}, $A_{0,KJ} = 10^{17.09}$ s^{-1} and when $b = 0.003$, $E_{vH} = 183.91$ kJ · mol^{-1}, $A_{0,vH} = 10^{20.53}$ s^{-1}.

(5) The critical temperature of thermal explosion of Keto-RDX is 448.68K.

(6) For Keto-RDX, the mathematic expression for the kinetic compensation effect may be written as

$$\lg A_{0,KJ} = 0.8197\ E_{KJ} - 133.344 \qquad r_{KJ} = 1.0$$

$$\lg A_{0,vH} = 0.2282\ E_{vH} - 21.436 \qquad r_{vH} = 1.0.$$

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[1] HU Rong-zu, GAO Sheng-li, ZHAO Feng-qi, et al. Thermal Analysis Kinetics (M). Beijing: Science Press, 2008: 54 - 302.

从恒速升温速率下的DSC曲线峰温计算含能材料放热分解反应动力学参数的理论和数值方法

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摘要: 根据Kooij公式和van't Hoff公式,从恒速升温速率下的DSC曲线峰温导出了计算含能材料放热分解反应动力学参数的两个数学表达式,提出了计算相应动力学参数的数值方法。对1,3,5-三硝基-1,3,5-三氮杂环己酮-2(Keto-RDX),由导出的两个表达式、Kissinger法、Ozawa法、Tang法、Hu-Gao-Zhang法、非线性等转化率积分法(NL-INT)所得的活化能E值彼此接近,表明Kooij's公式中的a值取0.5,van't Hoff公式的b值取0.003,可得到合理的动力学参数。

关键词: 物理化学; DSC; 动力学参数; Kooij公式; van't Hoff公式; Keto-RDX; 非等温

中图分类号: TJ55; O643 **文献标识码:** A

读者·作者·编者

《含能材料》征稿启事

一、征稿内容

(1) 炸药的合成与应用; 装药、成型、加工及其相关技术; (2) 炸药、推进剂、火工药剂、烟火剂及其应用技术; (3) 含能材料用聚合物、增塑剂及其相关物的合成与应用; (4) 含能材料的配方研制及相关技术; (5) 含能材料的性能检测技术(包括理化性能、爆轰性能、安全性能及其相容性); (6) 含能材料的储存寿命研究; (7) 爆炸技术及其应用; (8) 含能材料的环境适应性和力学性能; (9) 与含能材料有关的安全防护和环境保护技术; (10) 与本学科相关的科研动态、会议简讯、获奖信息、书评或新书介绍等报道性文章; (11) 有关科研机构的简要介绍。

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