Estimation of the kinetic parameters for thermal decomposition of HNIW and its adiabatic time-to-explosion by Kooij formula

Hong-xu GAO [a],[*], Feng-qi ZHAO [a], Rong-zu HU [a], Hong-an ZHAO [b], Hai ZHANG [c]

[a] Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Xi'an 710065, China
[b] College of Communication Science and Engineering, Northwest University, Xi'an 710069, China
[c] Department of Mathematics, Northwest University, Xi'an 710069, China

Abstract

A differential/integral method to estimate the kinetic parameters (apparent activation energy E_a and pre-exponential factor A) for thermal decomposition reaction of energetic materials based on Kooij formula are applied to study the nonisothermal decomposition reaction kinetics of hexanitrohexaazaisowurtzitane (HNIW) by analyzing nonisothermal DSC curve data. The apparent activation energy (E_a) obtained by the integral isoconversional non-isothermal method based on Kooij formula is used to check the constancy and validity of apparent activation energy by the differential/integral method based on Kooij formula. The most probable mechanism function of thermal decomposition reaction of HNIW is determined by a logical choice method. The equations for calculating the critical temperatures of thermal explosion (T_b) and adiabatic time-to-explosion (t_{TIad}) based on Kooij formula are used to calculate the values of T_b and t_{TIad} to evaluate the thermal safety and heat-resistant ability of HNIW. All the original data needed for analyzing the kinetic parameters are from nonisothermal DSC curves. The results show that the kinetic model function in differential form and the values of E_a and A of decomposition reaction of HNIW are $3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$, 152.73 kJ mol^{-1} and $10^{11.97}$ s^{-1}, respectively, and the values of self-accelerating decomposition temperature (T_{SADT}), T_b and t_{TIad} are 486.55 K, 493.11 K and 52.01 s, respectively.
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1. Introduction

According to the literature, addition of 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 2-hexaaza-tetracyclo-[5.5.0.0^{5,9}.0^{3,11}]-dodecane (HNIW or CL-20) to propellants or explosives is expected to increase the performance parameters such as specific impulse, ballistics and detonation velocity. In Ref. [1], the

kinetic parameters (apparent activation energy E_a and pre-exponential factor A) for nonisothermal thermal decomposition reaction and adiabatic time-to-explosion (t_{TIad}) of HNIW were presented based on Arrhenius formula $k = A\exp(-E/RT)$ (where E and A are constants). The results show that the kinetic model function in integral form and the value of E and A of the decomposition reaction of HNIW are $3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$, 155.04 kJ mol^{-1} and $10^{13.55}$ s^{-1}, respectively.

For studying thermal analysis kinetics and thermal safety of energetic materials, the kinetic parameters of nonisothermal thermal decomposition reaction and the values of t_{TIad} for HNIW are calculated based on Kooij formula [2], $k = A_0 T^B \exp(-E/RT)$, where A in $A = A_0 T^B$ is not strictly constant, but depends on T^B according to collision theory, and $B = 0.5$ [3].

* Corresponding author.
E-mail address: npecc@163.com (H.X. GAO).
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2. Theory and method for describing nonisothermal reaction kinetics based on the Kooij formula

2.1. Differential equation

The basic isothermal differential rate equation [3,4] describing the change of the conversion degree with time based on Kooij formula is

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) = A \exp\left(-\frac{E}{RT}\right)[1-\alpha(t)]^n$$

$$= A_0 T^B \exp\left(-\frac{E}{RT}\right)[1-\alpha(t)]^n \tag{1}$$

where α, t, A, A_0, B, E, T, n, R and $f(\alpha)$ have the usual meanings [3,4].

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

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

An overall equation for non-isothermal kinetics can be yielded by combining Eq. (1) with Eq. (2)

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

Differential of Eq. (3) with respect to T gives

$$\frac{d^2\alpha}{dT^2} = \frac{d\left(\frac{d\alpha}{dT}\right)}{dT} = \frac{d\left(\frac{A_0}{\beta}T^B e^{-E/RT} \cdot (1-\alpha(T))^n\right)}{dT}$$

$$= \frac{1}{\beta}\left(\frac{d\alpha}{dt}\right)\left[\frac{B}{T} + \frac{E}{RT^2} + n(1-\alpha(T))^{-1}\left(-\frac{d\alpha}{dT}\right)\right] \tag{4}$$

when

$$\left(\frac{d^2\alpha}{dT^2}\right)_{T=T_p, \alpha=\alpha_p} = 0 \tag{5}$$

the maximum reaction rate occurs. Eq. (4) gives

$$\frac{B}{T_p} + \frac{E}{RT_p^2} = n\left(1-\alpha_p\right)^{n-1}\frac{A_0}{\beta}T_p^B e^{-E/RT_p} \tag{6}$$

and

$$\beta = \frac{n\left(1-\alpha_p\right)^{n-1}A_0 T_p^B e^{-E/RT_p}}{\frac{B}{T_p} + \frac{E}{RT_p^2}} = \frac{n\left(1-\alpha_p\right)^{n-1}A_0 T_p^B e^{-E/RT_p}}{\frac{1}{T_p}\left(B + \frac{E}{RT_p}\right)}$$

$$= \frac{n\left(1-\alpha_p\right)^{n-1}A_0 T_p^{B+1} e^{-E/RT_p}}{B + \frac{E}{RT_p}} \tag{7}$$

where T_p and α_p are the peak temperature on DSC or DTG curve and the conversion degree at peak temperature, respectively.

By taking the natural logarithms on both sides of Eq. (7), we can obtain

$$\ln \beta = \ln n\left(1-\alpha_p\right)^{n-1} + \ln A_0 + (B+1)\ln T_p - \frac{E}{RT_p}$$

$$- \ln\left(B + \frac{E}{RT_p}\right) \tag{8}$$

Integration of Eq. (3) with the temperature between 0 and T, and the conversion degree between 0 and α results in

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta}\int_0^T T^B \exp\left(-\frac{E}{RT}\right)dT \tag{9}$$

Let

$$u = \frac{E}{RT} \tag{10}$$

we have

$$\int_0^T T^B \exp\left(-\frac{E}{RT}\right)dT = \left(\frac{E}{R}\right)^{B+1} \cdot \frac{e^{-u}}{u^{B+2}}\left[\frac{1}{u^0} - \frac{B+2}{u}\right.$$

$$+ \frac{(B+2)(B+3)}{u^2} - \frac{(B+2)(B+3)(B+4)}{u^3}$$

$$+ \ldots\left] \approx \left(\frac{E}{R}\right)^{B+1} \cdot \frac{e^{-u}}{u^{B+2}}\left[\frac{1}{u^0} - \frac{B+2}{u}\right]\right.$$

$$= \left(\frac{E}{R}\right)^{B+1} \cdot \frac{e^{-u}}{u^{B+2}}\left[\frac{u - (B+2)}{u}\right]$$

$$= \left(\frac{E}{R}\right)^{B+1} \cdot \frac{e^{-E/RT}}{\left(\frac{E}{RT}\right)^{B+2}}\left[\frac{\frac{E}{RT} - (B+2)}{\frac{E}{RT}}\right]$$

$$= \frac{RT^{B+2}}{E}\left[1 - \frac{(B+2)RT}{E}\right]e^{-E/RT} \tag{11}$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta}\frac{RT^{B+2}}{E}\left[1 - \frac{(B+2)RT}{E}\right]e^{-E/RT} \tag{12}$$

$$n \neq 1, \frac{1}{n-1}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] = \frac{A_0}{\beta}\frac{RT^{B+2}}{E}\left[1 - \frac{(B+2)RT}{E}\right]e^{-E/RT} \tag{13}$$

Eq. (6) becomes

$$\frac{RBT + E}{En(1-\alpha)^{n-1}} = \frac{A_0}{\beta}\frac{RT^{B+2}}{E}e^{-E/RT} \tag{14}$$

The following equation can be obtained by combining Eq. (6) with Eq. (13), $T = T_p$,

$$\frac{1}{n-1}\left[\frac{1}{(1-\alpha_p)^{n-1}} - 1\right] = \frac{RBT_p + E}{En(1-\alpha_p)^{n-1}}\left[1 - \frac{(B+2)RT_p}{E}\right] \tag{15}$$

From Eq. (15), we have

$$n\left[1-\left(1-\alpha_p\right)^{n-1}\right] = (n-1)\frac{RBT_p+E}{E}\left[1-\frac{(B+2)RT_p}{E}\right]$$

(16)

$$n\left[1-\left(1-\alpha_p\right)^{n-1}\right] = (n-1)\left(1+\frac{RBT_p}{E}\right)\left[1-\frac{(B+2)RT_p}{E}\right]$$

(17)

$$n\left(1-\alpha_p\right)^{n-1} = n-(n-1)\left(1+\frac{RBT_p}{E}\right)\left[1-\frac{(B+2)RT_p}{E}\right]$$

(18)

When

$$\frac{RBT_p}{E} << 1, \quad \frac{(B+2)RT_p}{E} << 1,$$

$$n\left(1-\alpha_p\right)^{n-1} \approx n-(n-1) = 1$$

(19)

The following equation can be obtained by combining Eq. (8) with Eq. (19)

$$\ln\beta = \ln A_0 + (B+1)\ln T_p - \frac{E}{RT_p} - \ln\left(B+\frac{E}{RT_p}\right)$$

(20)

The items on both the sides of Eq. (20) can be rearranged to obtain the following differential equation [3,4]

$$\ln\left[\frac{\beta_i\left(B+\frac{E}{RT_{pi}}\right)}{T_{pi}^{B+1}}\right] = \ln A_0 - \frac{E}{RT_{pi}}$$

(21)

For getting the values of E and A, the data (B, β_i, T_{pi}, $i=1$, $2,\ldots, L$) are fitted to Eq. (21) by the linear least-squares method.

2.2. Integral equation

The temperature integral using Frank-Kamenetskii's expression [6]

$$\int_0^T e^{-E/RT}dT = \frac{RT^2}{E}e^{-E/RT}$$

(22)

Integration of Eq. (3) with the temperature between 0 and T, and the conversion degree between 0 and α results in

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{[1-\alpha(T)]^n} = \frac{A_0}{\beta}\int_0^T T^B e^{-E/RT}dT = \frac{A_0R}{\beta E}\int_0^T T^{B+2}de^{-E/RT}$$

$$= \frac{A_0R}{\beta E}T^{B+2}e^{-E/RT}\left(1-(B+2)\frac{R}{E}T\right)^{B=\frac{1}{2}}$$

$$= \frac{A_0R}{\beta E}T^{\frac{5}{2}}e^{-E/RT}\left(1-\frac{5R}{2E}T\right)$$

(23)

Taking the logarithms on both sides of Eq. (23), the integral equation [Eq. (24)] [3,4] can be obtained

$$\ln\left[\frac{G(\alpha)}{T^{B+2}\left(1-(B+2)\frac{RT}{E}\right)}\right]^{B=\frac{1}{2}} = \ln\left[\frac{G(\alpha)}{T^{\frac{5}{2}}\left(1-\frac{5}{2}\frac{RT}{E}\right)}\right]$$

$$= \ln\left(\frac{A_0R}{\beta_i E}\right) - \frac{E}{RT}$$

(24)

Eq. (24) may be solved by the iterative method. Any arbitrary value may be assumed for E ($E > 0$), and this arbitrary value, original data (B, β_i, T_i, α_i, $i = 1,2,\ldots,L$) and any given $G(\alpha)$ can be used to calculate the value on the left-hand side of the expression for each data point. When a curve of the left-hand side of Eq. (24) against ($1/T$) is plotted by the linear least-squares method, new values of E from the slope and A_0 from the intercept are given. 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, the consistent values of E and A_0 will be obtained.

2.3. Model-free integral isoconversional non-linear equation [NL-INT-B] based on Kooij formula

According to the integral non-isothermal kinetic equation based on Kooij formula

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

(25)

and Eq. (25) can be written for a given conversion and a set of experiments performed under different heating rates as

$$\frac{A}{\beta_1}T_{\alpha,1}^B(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})$$

$$= \frac{A}{\beta_2}T_{\alpha,2}^B(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2}) = \cdots$$

$$= \frac{A}{\beta_n}T_{\alpha,n}^B(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})$$

(26)

we have

$$\Omega_{KI}(E_\alpha) = \min\left|\sum_{i=1}^n \sum_{j\neq i}^n \frac{\beta_j\cdot T_{\alpha,i}^B(T_{\alpha,i}-T_{0,i})\exp(-E_\alpha/RT_{\alpha,i})}{\beta_i\cdot T_{\alpha,j}^B(T_{\alpha,j}-T_{0,j})\exp(-E_\alpha/RT_{\alpha,j})}\right.$$

$$\left. - n(n-1)\right|$$

(27)

Eq. (27) [5,7] is known as the integral isoconversional non-linear equation based on Kooij formula (NL-INT-B method) for calculating E_α. The value of E_α calculated using Eq. (27) is used to check the validity of activation energy.

2.4. Adiabatic time-to-explosion equation based on Kooij formula

Under the adiabatic condition, the differential equation describing the time−temperature relation of this exothermal decomposition with Kooij's temperature dependence is

$$C_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t}=Qf(\alpha)A_0T^B\exp(-E/RT) \tag{28}$$

where C_{p}, Q, A_0 and E are the specific heat capacity, heat of reaction, pre-exponential constant and activation energy, respectively, R is the gas constant, T is the absolute temperature, t is the time, and α is the fraction of substance decomposed and can be expressed as a function of temperature

$$\alpha=\int_{T_0}^{T}\frac{C_{\mathrm{p}}}{Q}\mathrm{d}T=\int_{T_0}^{T}\frac{a+bT}{Q}\mathrm{d}T \tag{29}$$

where $C_{\mathrm{p}}=a+bT$. On rearranging and integrating Eq. (28), we obtain

$$t=\frac{1}{QA_0}\int_{T_0}^{T}\frac{a+bT}{T^Bf(\alpha)}\mathrm{e}^{E/RT}\mathrm{d}T \tag{30}$$

Eq. (30) is known as the adiabatic time-to-explosion equation based on Kooij formula. Once the values of a, b, Q, A, E, $T_{\mathrm{e}0}$ and T_{b}, are calculated from an analysis of the DSC curves, the correspondent value of t can then be obtained from Eq. (30).

2.5. Critical temperature of thermal explosion (T_b)

The value of T_{b} can be calculated by Eq. (31) [4,5]

$$\left(\frac{B}{T_{\mathrm{b}}}+\frac{E}{RT_{\mathrm{b}}^2}\right)(T_{\mathrm{b}}-T_{\mathrm{e}0})=1 \tag{31}$$

It may also be expressed as

$$T_{\mathrm{b}}=\frac{E-\sqrt{E^2-4R(1-B)(BR+E)T_{\mathrm{e}0}}}{2R(1-B)} \tag{32}$$

In Eq. (32), the value of $T_{\mathrm{e}0}$ ($=T_{\mathrm{SADT}}$) corresponding to $\beta\rightarrow 0$ may be obtained by using linear regression of $T_{\mathrm{e}i}$ and β_i as described in Eq. (33)

$$T_{\mathrm{e}i\,\mathrm{or}\,\mathrm{p}i}=T_{\mathrm{e}0\,\mathrm{or}\,\mathrm{p}0}+a_1\beta_i+a_2\beta_i^2+a_3\beta_i^3+\ldots+a_{L-2}\beta_i^{L-2}$$
$$\mathrm{i}=1,2,3\ldots L \tag{33}$$

3. Calculation example

3.1. Calculation of nonisothermal decomposition reaction kinetics

A multiple heating method [Eq. (21)] is employed to obtain the kinetic parameters (apparent activation energy E and pre-exponential constant A_0) by Kooij formula. From the original data [1] in Table 1, the values of E and A_0 obtained by Eq. (21) are determined to be 154.40 kJ mol^{-1} and $10^{12.09}$ s^{-1}, respectively. The linear correlation coefficient r is 0.9982.

By substituting the original data [1], β_i, T_{0i}, T_i, α_i, $i=1,2,\ldots,n$, tabulated in Table 2 from DSC curves into Eq. (27), the values of E_α for any given value of α in Table 3 are

Table 1
Initial temperature (T_0), onset temperature (T_{e}) and maximum peak temperature (T_{p}) of exothermic decomposition reaction for CL-20 determined by DSC curves at various heating rates (β).

β/(K min^{-1})	2	5	10	20
T_0/K	473.20	483.05	491.58	498.56
T_{e}/K	491.73	501.31	509.24	519.02
T_{p}/K	502.16	515.73	524.19	533.36

obtained. The $E_\alpha-\alpha$ curve is shown in Fig. 1. It shows that the activation energy changes slightly in the range from 0.125 to 0.875, which is properly selected to calculate the non-isothermal reaction kinetics. The average value of E_α in the range of α from 0.125 to 0.875 in Fig. 1 is 152.91 kJ mol^{-1}.

Eq. (24) is cited to obtain the values of E, A and the most probable kinetic model function [$f(\alpha)$] from each non-

Table 2
Data of HNIW determined by DSC.

Data point	α_i	T_i/K			
		$\beta=2$ (K min^{-1})	$\beta=5$ (K min^{-1})	$\beta=10$ (K min^{-1})	$\beta=20$ (K min^{-1})
1	0.025	488.29	499.59	508.08	516.02
2	0.050	490.63	502.22	510.46	518.78
3	0.075	491.96	503.83	512.03	520.49
4	0.100	492.97	504.98	513.19	521.77
5	0.125	493.75	505.88	514.13	522.82
6	0.150	494.45	506.67	514.93	523.69
7	0.175	495.06	507.35	515.63	524.47
8	0.200	495.61	507.96	516.26	525.16
9	0.225	496.13	508.52	516.84	525.79
10	0.250	496.66	509.04	517.37	526.38
11	0.275	497.09	509.54	517.86	526.93
12	0.300	497.49	510.02	518.34	527.45
13	0.325	497.84	510.48	518.79	527.94
14	0.350	498.19	510.91	519.23	528.42
15	0.375	498.51	511.32	519.65	528.87
16	0.400	498.85	511.71	520.06	529.29
17	0.425	499.17	512.09	520.45	529.70
18	0.450	499.50	512.46	520.84	530.10
19	0.475	499.82	512.83	521.22	530.48
20	0.500	500.14	513.19	521.59	530.85
21	0.525	500.43	513.53	521.95	531.20
22	0.550	500.71	513.88	522.31	531.56
23	0.575	501.00	514.20	522.65	531.89
24	0.600	501.29	514.53	522.99	532.23
25	0.625	501.59	514.86	523.31	532.55
26	0.650	501.88	515.17	523.64	532.87
27	0.675	502.14	515.48	523.94	533.17
28	0.700	502.42	515.78	524.25	533.47
29	0.725	502.70	516.07	524.56	533.76
30	0.750	502.99	516.37	524.86	534.04
31	0.775	503.30	516.67	525.16	534.31
32	0.800	503.61	516.97	525.46	534.57
33	0.825	503.92	517.28	525.74	534.82
34	0.850	504.25	517.60	526.04	535.09
35	0.875	504.62	517.93	526.34	535.39
36	0.900	505.01	518.29	526.65	535.76
37	0.925	505.41	518.69	526.98	536.25
38	0.950	505.90	519.14	527.40	537.05
39	0.975	506.62	519.81	528.22	538.68
40	1.000	511.97	527.31	538.75	551.65

isothermal DSC curve. $f(\alpha)$ and $G(\alpha)$ in Eq. (24) are the differential and integral model functions, respectively.

Forty-one types of kinetic model functions [6] and the data in Table 2 are put into Eq. (24) for calculation, respectively. The values of E, A, linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d) (where $d = (1 − r)Q$) were obtained by the linear least-squares.

The kinetic parameters, E and A and the probable kinetic model functions selected by the logical choice method and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E = 80−250$ kJ mol^{-1}, lg $A = 7−30$ s^{-1}) together with their appropriate values of r, Q and d, obtained by Eq. (24) are presented in Table 4. These values E and lg A obtained from the each nonisothermal DSC curve are approximately in agreement with the values calculated by Eqs. (21) and (27). Therefore, a conclusion can be drawn that the reaction mechanism of main exothermal decomposition process of HNIW is classified as random nucleation and subsequent growth, $n = 1/3$, $m = 3$, and the most probable kinetic model function of the decomposition reaction is $G(\alpha) = [−\ln(1 − \alpha)]^{1/3}$, $f(\alpha) = 3(1 − \alpha)[−\ln(1 − \alpha)]^{2/3}$. Substituting $f(\alpha)$ with $3(1 − \alpha)[−\ln(1 − \alpha)]^{2/3}$, E with 152.73 kJ mol^{-1} and A with $10^{11.97}$ s^{-1} in Eq. (34), we have

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} T^B f(\alpha) \exp(-E/RT) \qquad (34)$$

We can now establish a kinetic equation of the exothermic decomposition process of HNIW as follows

$$\frac{d\alpha}{dT} = \frac{10^{12.45}}{\beta} T^{0.5} (1 - \alpha)[-\ln(1 - \alpha)]^{\frac{2}{3}} \exp\left(-1.837 \times 10^4 / T\right)$$

Table 3
Apparent activation energies of thermal decomposition of HNIW obtained using isoconversional method [Eq. (27)] and the data taken from Table 2.

No.	α	E_α/ (kJ mol^{-1})	No.	α	E_α/ (kJ mol^{-1})
1	0.025	161.05	21	0.525	151.70
2	0.050	160.96	22	0.550	151.40
3	0.075	159.36	23	0.575	151.38
4	0.100	158.33	24	0.600	151.31
5	0.125	157.04	25	0.625	151.47
6	0.150	156.51	26	0.650	151.52
7	0.175	155.89	27	0.675	151.50
8	0.200	155.44	28	0.700	151.61
9	0.225	155.18	29	0.725	151.77
10	0.250	155.35	30	0.750	152.09
11	0.275	154.97	31	0.775	152.62
12	0.300	154.53	32	0.800	153.20
13	0.325	153.90	33	0.825	153.89
14	0.350	153.34	34	0.850	154.60
15	0.375	152.74	35	0.875	155.46
16	0.400	152.50	36	0.900	156.08
17	0.425	152.19	37	0.925	156.09
18	0.450	152.02	38	0.950	154.90
19	0.475	151.91	39	0.975	150.24
20	0.500	151.86	40	1.000	116.43

Mean in the range of 0.125−0.875. $E_{\alpha=0.125\sim0.875} = 152.91$ kJ mol^{-1}.

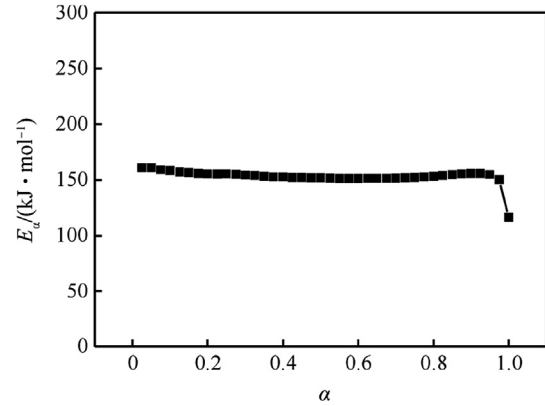Fig. 1. $E_\alpha − \alpha$ curves for the decomposition of HNIW by NL-INT-B method.

which is similar to the kinetic equation in Ref. [1] of the exothermic decomposition process of HNIW obtained by Arrhenius formula

$$\frac{d\alpha}{dT} = \frac{10^{14.03}}{\beta} (1 - \alpha)[-\ln(1 - \alpha)]^{\frac{2}{3}} \exp\left(-1.8648 \times 10^4 / T\right).$$

The E values obtained with the integral and differential methods, and the integral isoconversional non-linear method based on Kooij formula and Arrhenius formula [1] are close to each other, showing that taking the value of B of 0.5 in $A = A_0 T^B$ is suitable for calculating the kinetic parameters by Kooij formula.

3.2. Self-accelerating decomposition temperature (T_{SADT})

The values of T_{e0} of 486.55 K and T_{p0} of 495.64 K are obtained by substituting the original data, β_i, T_{ei}, T_{pi}, $i = 1,2,…L$, in Table 1 into Eq. (33).

3.3. Critical temperature of thermal explosion (T_b)

The value of T_b of 493.11 K is obtained by substituting the values of E of 152,730 J mol^{-1}, T_{e0} of 486.55 K, $R = 8.314$ J mol^{-1} K^{-1} into Eq. (32).

3.4. Adiabatic time-to-explosion (t_{TIad})

By substituting the values of $C_p = 0.2472 + 0.002705992 \, T$ [1], differential mechanism function $f(\alpha) =$

Table 4
Kinetic parameters obtained for the decomposition process of HNIW ($B = 0.5$).

Method	β(K min^{-1})	Function no.	E/(kJ mol^{-1})	log A_0/(s^{-1})	r	Q
Eq. (24)	2	11	161.55	12.91	0.9998	0.000495
	5	11	148.90	11.54	0.9995	0.001715
	10	11	150.45	11.73	0.9993	0.002483
	20	11	150.03	11.71	0.9983	0.006025
Mean	$E = 152.73$(kJ mol^{-1}), log A_0/(s^{-1}) $= 11.97$					
Eq. (21)			154.40	12.09	0.9982	0.009341

$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}, E = 152{,}730 \, \mathrm{J \, mol^{-1}}, A_0 = 10^{11.97} \, \mathrm{s^{-1}}$, decomposition heat $Q = 2340 \, \mathrm{J \, g^{-1}}, R = 8.314 \, \mathrm{J \, mol^{-1} \, K^{-1}}, \alpha$, conversion degree $\alpha = \int_{T_0}^{T} C_\mathrm{p}/Q \mathrm{d}T$, integral upper limit, $T = T_\mathrm{b} = 493.11$ K for t_TIad and integral lower limit, $T_0 = T_\mathrm{e0} = 486.55$ K into Eq. (32), The calculated value of t_Tlad of HNIW is 52.01 s.

4. Conclusions

1) A differential and an integral method are proposed for estimation of the kinetic parameters and mechanism function of thermal decomposing reaction of energetic materials by use of the Kooij equation. The differential method is based on the data acquired for a reaction investigated under various heating rates and may be considered as a new multiple scan method. Taking the value of B of 0.5 in $A = A_0 T^B$ is suitable for calculating the kinetic parameters by Kooij formula.

2) Using differential and integral equations, the kinetic parameters and the kinetic model function in integral form for the exothermic decomposition reaction of HNIW are $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$, 152.73 kJ mol^{-1} and $10^{11.97}$ s^{-1}, respectively. The kinetic equation of the exothermic decomposition reaction of HNIW can be described as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{10^{12.45}}{\beta} T^{0.5} (1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}} \exp\left(-1.837 \times 10^4/T\right)$$

3) The values of T_SADT, T_b and t_TIad of HNIW are 486.55 K, 493.11 K and 52.01 s, respectively, showing that HNIW has better thermal safety and heat-resistant ability.

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