Non-isothermal thermal decomposition reaction kinetics of 2-nitroimino-5-nitro-hexahydro-1,3,5-triazine (NNHT)

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ABSTRACT

The thermal behavior and decomposition reaction kinetics of 2-nitroimino-5-nitro-hexahydro-1,3,5-triazine (NNHT) were investigated by TG–DTG and DSC under atmospheric pressure and flowing nitrogen gas conditions. The results show that the thermal decomposition process of NNHT has two mass loss stages. The exothermic decomposition reaction mechanism obeys chemical reaction rule. The kinetic parameters of the reaction are $E_a = 131.77\,kJ\,mol^{-1}$, $\lg(A/s^{-1}) = 12.56$, respectively. The kinetic equation can be expressed as: $d\alpha/dt = 10^{12.86}(1-\alpha)^{3/2}\,e^{-1.5849 \times 10^4/T}$. The critical temperature of thermal explosion of NNHT obtained from the peak temperature (T_p) is $T_{bp} = 467.22\,K$. The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) of the reaction are $-7.978\,J\,mol^{-1}\,K^{-1}$, $127.99\,kJ\,mol^{-1}$ and $131.62\,kJ\,mol^{-1}$, respectively.

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1. Introduction

2-Nitroimino-5-nitro-hexahydro-1,3,5-triazine (NNHT) is a new energetic material containing two –NO_2 groups, two –NH_2 groups (Fig. 1) and hydrogen bonds of intramolecularly and inter-molecularly with higher energy and lower sensitivity. Its crystal density, detonation velocity and specific impulse are $1.88\,g\,cm^{-3}$, $9094\,m\,s^{-1}$ and $238\,s$, respectively [1,2]. It has the potential for possible use as an energy ingredient of gun propellants and explosives from the point of view of the above-mentioned high performance. It was used in formulation of tri-base gun propellant M30A1 and made the flame temperature of the propellant decrease and the powder force increase [3]. Its synthesis [4], crystal structure and molecular geometries [5] have been reported. In the present work, we reported its kinetic model function and kinetic parameters of the exothermic decomposition reaction with TG–DTG.

2. Experimental

2.1. Sample

2-Nitroimino-5-nitro-hexahydro-1,3,5-triazine used in this work (Fig. 1) was prepared and purified at Xi'an Modern Chemistry Research Institute. The structure of NNHT was characterized by elemental analyses, IR spectrometry and unclear magnetic resonance spectrometry. Its purity is more than 99.0%. Anal. Calcd (%) for $C_3H_6N_6O_4$: C, 18.95; N, 44.20; H, 3.18; Found (%): C, 19.69; N, 43.80; H, 3.22. IR (KBr, $\nu\,cm^{-1}$): 3330, 3216 (NH); 3123, 3047, 2972 (CH); 1607 (C–N); 1572 (NO_2). The sample was kept in a vacuum desiccator before use.

2.2. Equipment and conditions

TG–DTG and DSC curves under the condition of flowing nitrogen gas (99.999% purity; flowing rate, $60\,cm^3\,min^{-1}$; atmospheric pressure) were obtained by using a TA2950 thermal analyzer (TA Co., USA) and a TA 910S differential scanning calorimeter (TA Co., USA), respectively. The conditions of TG–DTG were as follows: sample mass, about 1 mg; heating rates (β), 2, 5, 10 and $15\,K\,min^{-1}$; reference sample, α-Al_2O_3. The conditions of DSC analyses were: sample mass, about
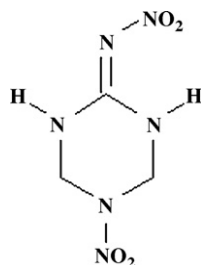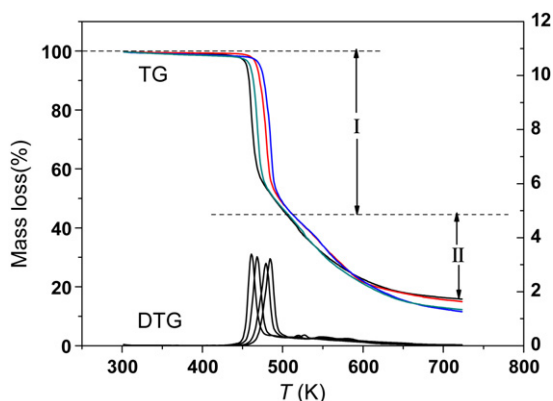
Fig. 1. The scheme of NNHT.

Fig. 2. TG–DTG curves for sample at different heating rates.

1 mg; heating rate, 10 K min^{-1}; reference sample, α-Al$_2$O$_3$. Heating rate is calculated according to the actual rate of temperature rise from room temperature to the temperature at the end of decomposition.

3. Results and discussion

3.1. The thermal decomposition behavior of NNHT

The TG–DTG curves at different heating rates and DSC curve at a heating rate of 10 K min^{-1} of sample are shown in Figs. 2 and 3, respectively. The results show that there are two mass loss stages (stages I and II) in TG curves, corresponding two peaks in DTG curves. From DSC curve, an exothermic peak, begins at 443.17 K and stops at 749.79 K, with summit peak at 481.88 K. For the TG curve when $\beta = 10$ K min^{-1}, stage I begins at 444.25 K and stops at 516.63 K, accompanied with 56.70% mass loss. Stage II begins at 516.63 K and stops at 744.12 K, with summit peak at 582.22 K,
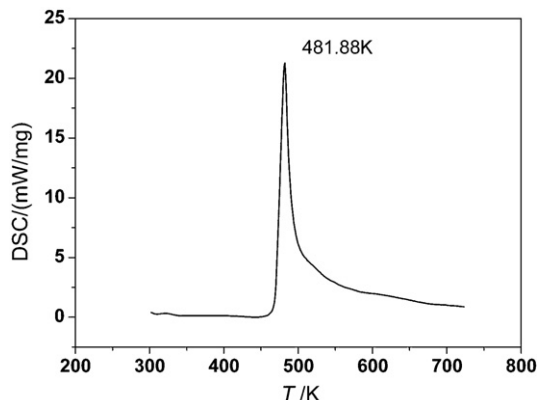
Table 1
Maximum peak temperature (T_p) of the exothermic decomposition reaction for NNHT determined by the TG–DTG curves at various heating rates (β).

β (K min^{-1})	T_p (K)
2	461.18
5	468.15
10	479.09
15	484.40

accompanied with 28.96% mass loss. There are a few remains at the end of decomposition. Stage I is caused by the main exothermic decomposition reaction.

3.2. The calculation of non-isothermal reaction kinetics

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the exothermic decomposition reaction for NNHT and check the constancy of activation energy by the single non-isothermal TG–DTG curve method, the two model-free isoconversional methods [Eqs. (1) and (2)] were employed. These methods are as follows:

Differential method:
Kissinger equation [6]:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{A_K R}{E} - \frac{E_K}{R T_p} \qquad (1)$$

Integral methods:
Flynn–Wall–Ozawa (FWO) equation [7]:

$$\lg \beta = \lg \left(\frac{A E_O}{R G(\alpha)} \right) - 2.315 - 0.4567 \frac{E_O}{RT} \qquad (2)$$

where α is the conversion degree, T the absolute temperature, E_α the apparent activation energy, β the heating rate, R the gas constant, T_p the peak temperature of DTG curve, E the apparent activation energy, A the pre-exponential factor, subscript K: data obtained by Kissinger's method, subscript O: data obtained by FWO method, and $G(\alpha)$ the integral mechanism function.

From the original data in Table 1, the value of E_K obtained by Kissinger's method [Eq. (1)] was determined to be 146.55 kJ mol^{-1} and A 10$^{14.09}$ s^{-1}, with linear correlation coefficient (r_k) being 0.9870. The values of E_O and r_O obtained by Ozawa's method [Eq. (2)] are 146.83 kJ mol^{-1} and 0.9883, respectively.

By substituting the original data, β_i, T_i and α_i, $i = 1, 2, \ldots n$, tabulated in Table 2 from TG–DTG curves into Eq. (2), the values of E_α for any given value of α in Table 2 were obtained. The average value of E_α in the α range of 0.40–0.80 in Fig. 4 is in good agreement with the calculated values obtained by Kissinger's method. The E values

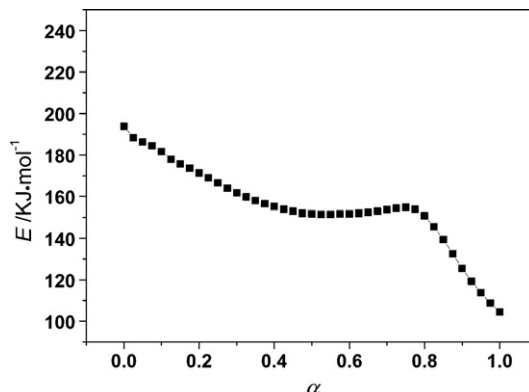Fig. 3. DSC curve for sample at a heating rate of 10 K min^{-1}.

Fig. 4. The $E_a \sim \alpha$ curve obtained by Ozawa's method.

Table 2
Data of NNHT determined by TG–DTG.

No.	α	$\beta = 2\,\mathrm{K\,min^{-1}}$	$\beta = 5\,\mathrm{K\,min^{-1}}$	$\beta = 10\,\mathrm{K\,min^{-1}}$	$\beta = 15\,\mathrm{K\,min^{-1}}$
		T_i/K	T_i/K	T_i/K	T_i/K
1	0.025	447.11	453.64	461.57	465.73
2	0.050	452.63	458.17	465.42	470.54
3	0.075	454.68	460.16	467.51	472.91
4	0.100	455.88	461.41	469.04	474.45
5	0.125	456.71	462.30	470.18	475.72
6	0.150	457.36	463.03	471.02	476.68
7	0.175	457.90	463.70	471.81	477.52
8	0.200	458.33	464.35	472.66	478.27
9	0.225	458.71	464.94	473.43	478.98
10	0.250	459.05	465.41	474.14	479.62
11	0.275	459.37	465.81	474.81	480.25
12	0.300	459.69	466.20	475.41	480.87
13	0.325	459.98	466.60	475.99	481.44
14	0.350	460.27	466.98	476.55	481.99
15	0.375	460.55	467.37	477.05	482.51
16	0.400	460.82	467.73	477.53	483.00
17	0.425	461.09	468.09	477.99	483.48
18	0.450	461.36	468.44	478.43	483.94
19	0.475	461.64	468.78	478.85	484.39
20	0.500	461.92	469.13	479.27	484.72
21	0.525	462.21	469.46	479.68	485.06
22	0.550	462.51	469.79	480.07	485.37
23	0.575	462.83	470.13	480.47	485.67
24	0.600	463.17	470.49	480.86	486.01
25	0.625	463.54	470.87	481.25	486.38
26	0.650	463.94	471.29	481.65	486.77
27	0.675	464.40	471.77	482.05	487.21
28	0.700	464.90	472.32	482.51	487.69
29	0.725	465.46	472.97	483.03	488.24
30	0.750	466.08	473.75	483.75	488.91
31	0.775	466.79	474.71	484.74	489.87
32	0.800	467.60	475.97	486.13	491.32
33	0.825	468.52	477.64	488.00	493.36
34	0.850	469.64	479.92	490.33	495.95
35	0.875	470.99	482.69	493.15	499.10
36	0.900	472.65	485.93	496.59	502.74
37	0.925	474.79	489.47	500.54	506.88
38	0.950	477.43	493.34	504.94	511.53
39	0.975	480.33	497.42	509.57	516.59

calculated using Eq. (2) were used to check the validity of activation energy by the other methods.

The integral Eqs. (3)–(7) were cited to obtain the values of E_α, A and the most probable kinetic model function $f(\alpha)$ from a single non-isothermal TG–DTG curve [8,9].

Ordinary-integral equation:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{3}$$

MacCallum–Tanner equation [10]:

$$\lg[G(\alpha)] = \lg\left(\frac{AE_a}{\beta R}\right) - 0.4828 E_a^{0.4357} - \frac{0.449 + 0.217 E_a}{0.001}\frac{1}{T} \tag{4}$$

Šatava–Šesták equation [11]:

$$\lg = [G(\alpha)] = \lg\left(\frac{AE_a}{\beta R}\right) - 2.315 - 0.4567\frac{E_a}{RT} \tag{5}$$

Coats–Redfern equation [12]:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{6}$$

Madhusudanan–Krishnan–Ninan equation [13]:

$$\ln\left[\frac{G(\alpha)}{T^{1.921503}}\right] = \left[\ln\frac{AE}{\beta R} + 3.772050 - 1.921503\ln E\right]$$
$$- 0.120394\left(\frac{E}{T}\right) \tag{7}$$

Forty-one types of kinetic model functions in Ref. [14] and the data, α, T, and T_0 from TG–DTG curves under various linear heating rates β in Table 2 were put into Eqs. (3)–(7) for calculation, respectively. The values of E_a, 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 [9].

The most probable mechanism function was selected by the better values of r, and Q based on the following four conditions: (1) the values of $E_a/(\mathrm{kJ\,mol^{-1}})$ and $\lg(A/\mathrm{s^{-1}})$ selected are in the ordinary range of the thermal decomposition kinetic parameters for solid materials [$E_a/(\mathrm{kJ\,mol^{-1}}) = 80$–$250$ and $\lg(A/\mathrm{s^{-1}}) = 7$–$30$]; (2) linear correlation coefficient (r) is greater than 0.98; (3) the values

Table 3
Kinetic parameters obtained for the decomposition process of sample.

Method	β (K min^{-1})	E_a (kJ mol^{-1})	$\lg(A/\mathrm{s^{-1}})$	r	Q
Ordinary-integral	2	139.84	13.41	0.9994	0.000463
	5	123.19	11.65	0.9964	0.00291
	10	126.46	12.01	0.9952	0.003922
	15	136.39	13.12	0.9939	0.0004963
MacCallum–Tanner	2	139.95	13.36	0.9995	0.0000868
	5	123.31	11.60	0.9968	0.000548
	10	126.76	11.98	0.9957	0.0007396
	15	136.86	13.12	0.9946	0.000935
Šatava–Šesták	2	140.32	13.45	0.9995	0.0000868
	5	124.60	11.80	0.9968	0.000548
	10	127.87	12.16	0.9957	0.0007396
	15	137.40	13.22	0.9946	0.000935
Coats–Redfern	2	139.84	13.39	0.9994	0.000463
	5	123.19	11.62	0.9965	0.00291
	10	126.46	11.98	0.9952	0.003922
	15	136.39	13.10	0.9939	0.004963
Madhusudanan–Krishnan–Ninan	2	140.01	13.43	0.9994	0.000463
	5	123.37	11.67	0.9964	0.00291
	10	126.64	12.03	0.9950	0.003922
	15	136.57	13.14	0.9940	0.004963
Mean		131.77	12.56		
Kissinger		146.55	14.09	0.9870	0.05464
Flynn–Wall–Ozawa		146.83		0.9883	0.001027

of $E_a/(\text{kJ mol}^{-1})$ and $\lg(A/\text{s}^{-1})$ obtained with the differential and integral methods are approximately the same; (4) the mechanism function selected must be in agreement with the tested sample state. The results of satisfying the conditions mentioned above were listed in Table 3.

The values of $E_a/(\text{kJ mol}^{-1})$ and $\lg(A/\text{s}^{-1})$ obtained from a single non-isothermal DTG curve are in good agreement approximately with the values calculated by Kissinger's method and Ozawa's method. Therefore, conclusion could be drawn as that the reaction mechanism of the main exothermic decomposition process of the sample is classified as chemical reaction, and the mechanism function $G(\alpha)=(1-\alpha)^{-1/2}$, $f(\alpha)=2(1-\alpha)^{3/2}$. Substituting $f(\alpha)$ with $2(1-\alpha)^{3/2}$, $E_a/\text{kJ mol}^{-1}$ with 131.77 and $\lg(A/\text{s}^{-1})$ with 12.56 into Eq. (8):

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \qquad (8)$$

and the kinetic equation of exothermal decomposition reaction may be described as:

$$\frac{d\alpha}{dt} = 10^{12.86}(1-\alpha)^{3/2}e^{-1.5849\times10^4/T}. \qquad (9)$$

The values (T_{po}) of peak temperature (T_p) corresponding to $\beta \to 0$ obtained by Eq. (10) taken from Ref. [15] are 454.86 K.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2, \quad i = 1-4 \qquad (10)$$

where b and c are coefficients.

The corresponding critical temperatures of thermal explosion (T_{bp}) obtained from Eq. (11) taken from Ref. [15] are 467.22 K.

$$T_{bp} = \frac{E_O - \sqrt{E_O^2 - 4E_O RT_{p0}}}{2R} \qquad (11)$$

where R the gas constant ($8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$), E_O the value of E_a by Ozawa's method.

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) corresponding to $T = T_{p0}, E_a = E_K$ and $A = A_k$ obtained by Eqs. (12)–(14) [14] are $-7.978\,\text{J mol}^{-1}\,\text{K}^{-1}$, $127.99\,\text{kJ mol}^{-1}$ and $131.62\,\text{kJ mol}^{-1}$, respectively. The activation Gibbs free energy ($\Delta G^{\neq}$) is positive, so the exothermic decomposition reaction for NNHT must proceed under the condition of heating.

$$A = \frac{k_B T}{h}e^{\Delta S^{\neq}/R} \qquad (12)$$

$$\Delta H^{\neq} = E_a - RT \qquad (13)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (14)$$

where k_B the Boltzmann constant ($1.3807 \times 10^{-23}\,\text{J K}^{-1}$), and h the Plank constant ($6.626 \times 10^{-34}\,\text{J s}^{-1}$).

4. Conclusions

(1) The kinetics of the exothermic decomposition reaction for NNHT has been investigated. The kinetic model function in an integral form, apparent activation energy and pre-exponential constant of this reaction are $(1-\alpha)^{-1/2}$, $131.77\,\text{kJ mol}^{-1}$ and $10^{12.56}\,\text{s}^{-1}$, respectively.

(2) The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of this reaction at T_{p0} are $-7.978\,\text{J mol}^{-1}\,\text{K}^{-1}$, $127.99\,\text{kJ mol}^{-1}$ and $131.62\,\text{kJ mol}^{-1}$, respectively.

(3) The critical temperature of thermal explosion of the compound is 467.22 K.

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