Kinetics of the Exothermic Decomposition Reaction of *N*-Methyl-*N*-nitro-2,2,2-trinitroethanamine

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The thermal behavior and kinetic parameters of the exothermic decomposition reaction of *N*-methyl-*N*-nitro-2,2,2-trinitroethanamine in a temperature-programmed mode have been investigated by means of differential scanning calorimetry (DSC). The kinetic equation of the exothermic decomposition process of the compound is proposed. The values of the apparent activation energy (E_a), pre-exponential factor (A), entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) of this reaction and the critical temperature of thermal explosion of the compound are reported. Information is obtained on the mechanism of the initial stage of the thermal decomposition of the compound.

Keywords decomposition, *N*-methyl-*N*-nitro-2,2,2-trinitroethanamine, kinetic, mechanism

Introduction

N-Methyl-*N*-nitro-2,2,2-trinitroethanamine is a typical nitramine. Its crystal density is 1.80 $g \cdot cm^{-3}$. The detonation velocity corresponding to $\rho = 1.787\ g \cdot cm^{-3}$ is about 8732 $m \cdot s^{-1}$. Its energy is high as that of cyclotrimethylenenitramine (RDX). Therefore, it is used as high explosive. Its thermal behavior[1] and explosion properties[2] have been reported. In this present work, we report its kinetic parameters of the exothermic decomposition reaction studied with differential scanning calorimetry (DCS). This is quite useful in the evaluation of its thermal stability under non-isothermal condition and in the study of its thermal changes at high temperature.

Experimental

N-Methyl-*N*-nitro-2,2,2-trinitroethanamine used in this work was prepared in Xi'an Modern Chemistry Research Institute. m.p. > 84.5 ℃; ^{1}H NMR (90 MHz, $CDCl_3$) δ: 3.62 (s, 3H, CH_3), 5.94 (s, 2H, CH_2); IR (KBr) ν: 1638, 1300 (N—NO_2), 1550, 1360 (C—NO_2), 870 (C—N), 820 (N—O), 2975 (CH_3), 2925 (CH_2) cm^{-1}; MS m/z: 239 (M^+). Anal. calcd for $C_3H_5N_5O_8$: C 15.07, H 2.11, N 29.29; found C 14.94, H 2.20, N 28.95. Its purity was more than 99.5 %. The sample was kept in a vacuum desiccator before use.

DSC experiments were carried out with a Model CDR-1 thermal analyzer made in Shanghai Balance Instrument Factory, using Ni/Cr-Ni/Si thermocouple plate and working in static air with heating rates of 1—20 ℃·min^{-1}. α-Al_2O_3 was used as reference material. 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.

Results and discussion

Typical DSC curve of the title compound is shown in Fig. 1. DSC curve shows an endothermic peak at its melting point (84.5 ℃) with summit peak at 85.0 ℃. An exothermic peak at 189 ℃ is due to decomposition of TNMA in molten state.

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the exothermic decomposition reaction for the title compound, a multiple heating method (Kissinger 's method) was employed.[3] From the original data in Table 1, the apparent activation energy (E_k) obtained by Kissinger 's me-

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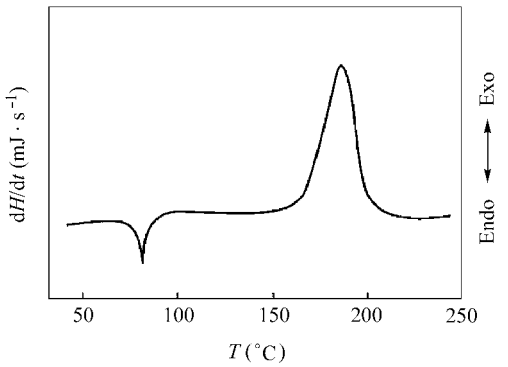


Fig. 1 DSC curve of the title compound at a heating rate of 10 ℃·min^{-1}.

thod is 123.2 kJ·mol^{-1} and A is $10^{12.16}$ s^{-1}. The linear correlation coefficient (r_k) is 0.9818. The values of E_0 and r_0 obtained by Ozawa's method[4] are 124.3 kJ·mol^{-1} and 0.9838, respectively.

Table 1 Maximum peak temperature (T_p) of the exothermic decomposition reaction for the title compound determined by the DSC curves at various heating rates (β)

β (℃·min^{-1})	1.1743	2.0513	5.2174	10.7143	22.2727
T_p (℃)	157	164	174	189	191

The integral Eqs. (1),[5] (2),[6] (3),[7] (4)[8] and (5),[5] and the differential Eqs. (6)[9] and (7)[10] are cited to obtain the values of E_a, A and the most probable kinetic model function [$f(\alpha)$] from a single non-isothermal DSC curve.[11]

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

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

$$\ln[G(\alpha)] = \ln\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4357} - \frac{0.449+0.217}{0.001}\frac{1}{T} \tag{3}$$

$$\ln[G(\alpha)] = \ln\left(\frac{AE}{\beta R}\right) - 2.315 - 0.4567\frac{E}{RT} \tag{4}$$

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

$$\ln\left\{\frac{\frac{d\alpha}{dT}}{f(\alpha)\left[\frac{E(T-T_0)}{RT^2}\right]}+1\right\} = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \tag{6}$$

$$\ln\left[\frac{d\alpha}{f(\alpha)dT}\right] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \tag{7}$$

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model function, respectively, T_0 is the initial point at which DSC curve deviates from the baseline, R the gas constant, α the conversion degree ($\alpha = H_t/H_o$), dH_t/dt the exothermic heat flow at time t, H_o the total heat effect (corresponding to the global area under the DSC curve), H_t the reaction heat at a certain time (corresponding to the partial area under the DSC curve), T the temperature (K) at time t.

Thirty types of kinetic model functions[12] and the data in Table 2 are put into Eqs. (1)—(7) for calculation, respectively. The values of E_a, A, linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d) [where $d = Q(1-r)$] were obtained by the linear least-squares and iterative methods.[4]

Table 2 Data of the title compound determined by DSC[a]

Data point	T_i(K)	α_i	$(dH_i/dt)_i$ (mJ·s^{-1})	$(d\alpha/dT)_i$ (10^2 K^{-1})
1	443.2	0.1163	0.8619	1.1378
2	445.2	0.1395	1.1046	1.4581
3	448.2	0.2209	1.5564	2.0547
4	451.2	0.2674	1.8828	2.4855
5	453.2	0.3256	2.4435	3.2256
6	457.2	0.4302	2.9539	3.8994
7	460.2	0.5116	3.4392	4.5401
8	463.2	0.6395	3.5815	4.7279

[a] T_o = 427.2 K; H_o = 431.79 mJ; β = 0.1754 ℃·s^{-1}.

The probable kinetic model functions of the integral and differential methods selected by the logical choice method[4] and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials (E = 80—250 kJ·mol^{-1}, log A = 7—30 s^{-1}) are $f(\alpha) = \frac{2}{3}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$ and $G(\alpha) = [-\ln(1-\alpha)]^{2/3}$, indicating that the reaction mechanism of the exothermic process of the title compound is classified as nucleation and growth, and the mechanism function is No. 14, the Avramic-Erofeev equation with $n = \frac{3}{2}$. Substituting $f(\alpha)$ with $\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, E with 112.48 kJ·mol^{-1}, β with 0.1754 K·s^{-1} and A with $10^{9.44}$ s^{-1} in Eq. (8).

$$d\alpha/dT = \frac{A}{\beta}f(\alpha)e^{-E/RT} \tag{8}$$

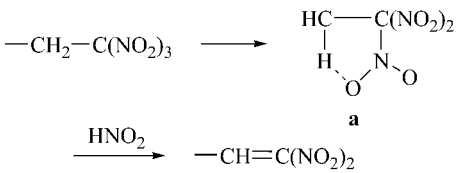
we can now establish the kinetic equation of the exothermic decomposition process of the title compound as follows:

$$\frac{d\alpha}{dT} = 10^{10.37}(1-\alpha)[-\ln(1-\alpha)]^{1/3}e^{-1.353\times10^4/T} \quad (9)$$

The corresponding kinetic parameters are summarized in Table 3.

The mean values of E_a and A obtaind by Eqs. (1)—(7) approach the calculated ones by Kissinger's method and Ozawa's method. The value of E_a is only 112.48 kJ·mol^{-1}, indicating that the activated complex **a** as shown in Scheme 1 could be formed during the decomposition.

Scheme 1



The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta\to0$ obtained by Eq. (10) taken from Ref. 13 is 152.37 ℃.

$$T_{pi} = T_{po} + b\beta_i + c\beta_i^2 + d\beta_i^3,\ i = 1—5 \quad (10)$$

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (11) taken from Ref. 13 is 165.22 ℃.

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{po}}}{2R} \quad (11)$$

where R is the gas constant (8.314 J·mol^{-1}·K^{-1}), E_0 is the value of E obtained 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 $T = T_{po}$, $E = E_k$ and $A = A_k$ obtained by Eqs. (12), (13) and (14) are −15.08 J·mol^{-1}·K^{-1}, 123.2 kJ·mol^{-1} and 129.6 kJ·mol^{-1}, respectively.

$$A = \frac{k_BT}{h}e^{\Delta S^{\neq}/R} \quad (12)$$

$$A\exp\left(-\frac{E}{RT}\right) = \frac{k_BT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(\frac{\Delta H^{\neq}}{RT}\right) \quad (13)$$

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

where k_B is the Boltzmann constant (1.3807×10^{-23} J·K^{-1}) and h the Planck constant (6.626×10^{-34} J·s).

Conclusions

The kinetic model function in differential form, apparent activation energy and pre-exponential constant of the exothermic decomposition reaction for *N*-methyl-*N*-nitro-2,2,2-trinitroethanamine are $\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, 112.48 kJ·mol^{-1} and $10^{9.44}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 165.22 ℃. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of the reaction at T_{po} are −15.08 J·mol^{-1}·K^{-1}, 123.2 kJ·mol^{-1} and 129.6 kJ·mol^{-1}, respectively.

Table 3 Kinetic parameters obtained by the data in Table 2

No.	Equation	Function No.[a]	E_a(kJ·mol^{-1})	log(A/s^{-1})	r	Q	$d\cdot10^5$
1	(1)	14	109.91	8.66	0.9957	0.0128	5.4895
2	(2)	14	109.91	8.69	0.9957	0.0128	5.4895
3	(3)	14	109.62	8.60	0.9963	0.0024	0.8979
4	(4)	14	111.68	8.90	0.9963	0.0024	0.8979
5	(5)	14	109.91	8.69	0.9957	0.0128	5.4895
6	(6)	14	100.22	9.00	0.9971	0.0070	2.0069
7	(7)	14	136.13	13.54	0.9975	0.0069	1.7304
Mean: E_a = 112.48 kJ·mol^{-1}, log(A/s^{-1}) = 9.44							

[a] Function No. 14: $f(\alpha) = \frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, $G(\alpha) = [-\ln(1-\alpha)]^{2/3}$.

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