Chinese Journal of Chemistry, **2004**, *22*, 658—660 **Article**

Thermal Behavior of *N*,*N'*-Bis[*N*-(2,2,2-trinitroethyl)-*N*-nitro]ethylenediamine

CHEN, San-Ping[a](陈三平) HU, Rong-Zu*[,a,b](胡荣祖) SONG, Ji-Rong[a](宋纪蓉)
YANG, De-Suo[c](杨得琐) GAO, Sheng-Li[a](高胜利) SHI, Qi-Zhen[a](史启祯)

[a] *Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, China*
[b] *Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, China*
[c] *Department of Chemistry & Chemical Engineering, Baoji College of Arts and Science, Baoji, Shaanxi 721007, China*

The thermal behavior and kinetic parameters of the exothermic decomposition reaction of *N*,*N'*-bis[*N*-(2,2,2-trinitroethyl)-*N*-nitro]ethylenediamine in a temperature-programmed mode have been investigated by means of differential scanning calorimetry (DSC). The results show that kinetic model function in differential form, apparent activation energy E_a and pre-exponential factor A of this reaction are $3(1-\alpha)^{2/3}$, 203.67 kJ•mol^{-1} and $10^{20.61}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 182.2 ℃. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of this reaction are 143.3 J•mol^{-1}•K^{-1}, 199.5 kJ•mol^{-1} and 135.5 kJ•mol^{-1}, respectively.

Keywords decomposition, *N*,*N*'-bis[*N*-(2,2,2-trinitroethyl)-*N*-nitro]ethylenediamine, kinetics

Introduction

N,*N'*-Bis[*N*-(2,2,2-trinitroethyl)-*N*-nitro]ethyenediamine (BTNEDA) is a typical nitramine compound, which is structurally shown in Figure 1. The crystal density is 1.87 g•cm^{-3}. The detonation velocity corresponding to ρ=1.842 g•cm^{-3} is about 8970 m•s^{-1}.[1] Therefore, BTNEDA is used as high explosive. Its thermogram has been reported.[2] In this paper, its kinetic parameters of the exothermic decomposition reaction are described. 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.

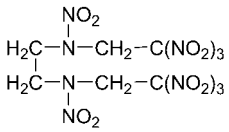


Figure 1 General structure of *N*,*N'*-bis[*N*-(2,2,2-trinitroethyl)-*N*-nitro]ethylenediamine.

Experimental

BTNEDA was prepared in Xi'an Modern Chemistry Research Institute. The structure of BTNEDA was characterized by elemental analyses, molecular weight determination, IR spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry and 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 1—20 ℃•min^{-1}. DSC curves were obtained with a sealed cell of aluminum (diameter 5 mm×3 mm). The amount of sample used was about 0.7 mg. The calorimetric sensitivities were ±0.92 and ±41.84 mJ•s^{-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 precision of temperature was 0.25 ℃. The temperature and heat were calibrated using indium and tin powders. DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of the tests was satisfactory.

Results and discussion

A typical DSC curve for BTNEDA is shown in Figure 2. DSC curve consists of one endothermic peak and one exothermic peak. The endothermic peak at 180 ℃ is the phase change from solid to liquid, while the exothermic peak at 197 ℃ is caused by the decomposition reaction.

In order to obtain the kinetic parameters (apparent activation energy E_a and pre-exponential factor A) of the

* E-mail: hurongzu@public.xa.sn.cn
Received September 8, 2003; revised December 19, 2003; accept March 15, 2004.
Project supported by the Science and Technology Foundation of Shaanxi Key Laboratory of Physico-Inorganic Chemistry (No. 29-3, 2001) and the Science and Technology Foundation of the National Defence Key Laboratory of Propellant and Explosive Combustion of China (No. 514550101).

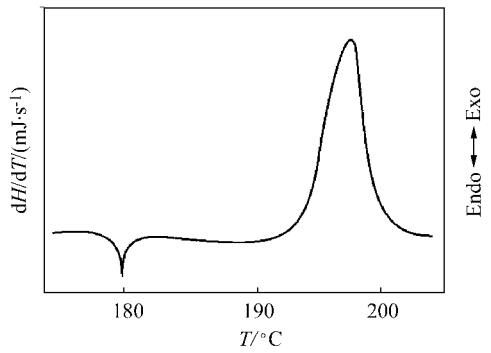


Figure 2 DSC curve for BTNEDA at a heating rate of 10 ℃•min^{-1}.

exothermic decomposition reaction for BTNEDA, a multiple heating method[3] (Kissinger's method) was employed. From the original data in Table 1, E_k and A were determined to be 199.5 kJ•mol^{-1} and $10^{20.45}$ s^{-1}, respectively. The linear correlation coefficient r_k is 0.9976. The values of E_0 and r_0 obtained by Ozawa's method[4] are 197.0 kJ•mol^{-1} and 0.9978, respectively.

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

β/(℃•min^{-1})	1.053	2.105	5.294	10.56	20.63
T_p/℃	177	184	190	197	203

The integral Eq. (1) and differential Eq. (2) 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.[5]

$$\ln\frac{G(\alpha)}{T-T_0}=\ln\frac{A}{\beta}-\frac{E_a}{RT} \quad (1)$$

$$\ln\frac{d\alpha/dT}{f(\alpha)[E_a(T-T_0)/RT^2+1]}=\ln\frac{A}{\beta}-\frac{E_a}{RT} \quad (2)$$

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model functions, respectively, T_0 is the initial point at which DSC curve deviates from the baseline, R the gas constant, α the conversion degree ($\alpha=H_t/H_0$), dH_t/dt the exothermic heat flow at time t, H_0 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,

$$\frac{d\alpha}{dt}=\frac{1}{H_0\beta}\frac{dH}{dt}$$

Thirty types of kinetic model functions[6] and the data in Table 2 are put into Eqs. (1) and (2) for calculation, respectively. The values of E_a, A, linear correlation coefficient r and standard mean square deviation Q were obtained by the linear least-squares and iterative methods.[5]

Table 2 Data of BTNEDA 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	439.05	0.0674	0.4519	1.8161
2	440.75	0.1032	0.6192	2.4888
3	442.55	0.1494	0.7448	2.9933
4	444.25	0.2078	0.9372	3.7668
5	445.95	0.2818	1.1184	4.7590
6	447.25	0.3478	1.3472	5.4148
7	448.55	0.4228	1.5272	6.1379
8	449.65	0.4922	1.6652	6.6928
9	450.55	0.5517	1.7531	7.0460
10	452.95	0.7282	1.9121	7.6850

[a] T_0=430.35 K; H_0=298.57 mJ; β=0.08333 ℃•s^{-1}.

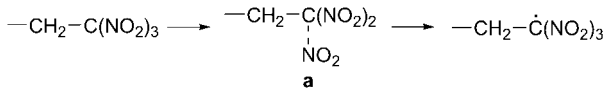
The probable kinetic model functions of the integral and differential methods selected by the logical choice method[5] and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials (E=80−250 kJ•mol^{-1}, log A=7−30 s^{-1}) are $f(\alpha)=3(1-\alpha)^{2/3}$ and $G(\alpha)=1-(1-\alpha)^{1/3}$, indicating that the reaction mechanism of the exothermic decomposition process of BTNEDA is classified as phase boundary reaction, R_3 with spherical symmetry. The corresponding kinetic parameters are summarized in Table 3. The kinetic equation of the exothermic decomposition process of BTNEDA may be described as $d\alpha/dT=10^{22.17}(1-\alpha)^{2/3}e^{-2.450\times10^4/T}$. The values of E_a and A obtained by Eqs. (1) and (2) are in good agreement with the calculated values by Kissinger's method and Ozawa's method. The value of E_a approaches the dissociation energy of the C—NO_2 bond (188.3 kJ•mol^{-1}),[7] and the rapture of the C—NO_2 bond within the trinitromethyl group is easier than that of the N—NO_2 bond in the molecule of the title compound,[8] indicating that the activated complex **a** as shown in Scheme 1 could be formed during the decomposition. In the activated complex **a**, a C—NO_2 bond is lengthened to a certain extent so that rupture of this bond is possible.

Table 3 Kinetic parameters obtained by the data in Table 2[a]

No.	Eq.	$f(\alpha)$	E/(kJ•mol^{-1})	log A	r	Q
1	1	$3(1-\alpha)^{2/3}$	209.11	21.23	0.9997	0.0017
2	2	$3(1-\alpha)^{2/3}$	198.23	19.98	0.9981	0.0099

[a] E=203.67 kJ•mol^{-1}, log A=20.61.

Scheme 1



a

The value T_{po} of the peak temperature T_p corresponding to $\beta\to0$ obtained by Eq. (3) taken from Ref. 9 is 173.4 ℃.

$$T_{pi}=T_{po}+b\beta_i+c\beta_i^2+d\beta_i^3 \qquad (i=1-5) \tag{3}$$

where b, c and d are coefficients.

The critical temperature T_b of thermal explosion obtained from Eq. (4) taken from Ref. 9 is 182.2 ℃.

$$T_b=\frac{E_0-\sqrt{E_0^2-4E_0RT_{po}}}{2R} \tag{4}$$

where R is the gas constant (8.314 J•mol^{-1}•K^{-1}), and 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. (5), (6) and (7) are 143.3 J•mol^{-1}•K^{-1}, 199.5 kJ•mol^{-1} and 135.5 kJ•mol^{-1}, respectively.

$$A=\frac{k_BT}{h}e^{\Delta S^{\neq}/R} \tag{5}$$

$$A\exp(-E/RT)=\frac{k_BT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{6}$$

$$\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq} \tag{7}$$

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).

Conclusion

The kinetic model function in differential form, apparent activation energy and pre-exponential constant of the exothermic decomposition reaction for BTNEDA are $3(1-\alpha)^{2/3}$, 203.67 kJ•mol^{-1} and $10^{20.61}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 182.2 ℃. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of the reaction at T_{po} are 143.3 J•mol^{-1}•K^{-1}, 199.5 kJ•mol^{-1} and 135.5 kJ•mol^{-1}, respectively.

References

1 Dong, H. S.; Zhou, F. F. *Properties of High Explosives and Related Materials*, Science Press, Beijing, **1989**, p. 281 (in Chinese).
2 Dong, H. S.; Hu, R. Z.; Yao, P. *Collection of Thermospectrum of Energetic Materials*, National Defence Industry Press, Beijing, **2001**, p. 7 (in Chinese).
3 Kissinger, H. E. *Anal. Chem*. **1957**, *29*, 1702.
4 Ozawa, T. *Bull. Chem. Soc. Jpn*. **1965**, *38*, 1881.
5 Hu, R. Z.; Yang, Z. Q.; Liang, Y. J. *Thermochim. Acta* **1988**, *123*, 135.
6 Hu, R. Z.; Shi, Q. Z. *Thermal Analysis Kinetics*, Science Press, Beijing, **2001**, p. 67 (in Chinese).
7 Yang, D. S. *M. S. Thesis*, Xi'an Modern Chemistry Research Institute, Xi'an, **1987** (in Chinese).
8 Zhang, H. S.; Hu, R. Z.; Yang, D. S. *Thermochim. Acta* **1990**, *165*, 235.
9 Zhang, T. L.; Hu, R. Z.; Xie, Y.; Li, F. P. *Thermochim. Acta* **1994**, *244*, 17.

(E0309081 LI, L. T.)