Kinetic Study on the Exothermic First-stage Decomposition Reaction of 2,4,8,10-Tetranitro-2,4,8,10-tetraaza-spiro[5,5]undecane-3,9-dione

HU, Rong-Zu(胡荣祖) *[a,b]   ZHAO, Feng-Qi[a](赵凤起)   WANG, Bo-Zhou[a](王伯周)
GAO, Sheng-Li[b](高胜利)   ZHU, Chun-Hua[a](朱春华)   NING, Bin-Ke[a](宁斌科)
CHEN, Pei[a](陈沛)   LUO, Yang[a](罗阳)   SONG, Ji-Rong[b](宋纪蓉)
SHI, Qi-Zhen[b](史启祯)

[a] Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, China
[b] Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, China

Under linear temperature increase condition the thermal behavior and kinetic parameters of the exothermic first-stage decomposition reaction of the title compound were studied by means of DSC and TG-DTG. The empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of this reaction are $\alpha^{0.122}(1-\alpha)^{0.528}$, 216.4 kJ•mol^{-1} and 1020.51 s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 222.25 ℃. The values of $\Delta^{\neq}S$, $\Delta^{\neq}H$, and $\Delta^{\neq}G$ and of this reaction are 108.3 J•mol^{-1}•K^{-1}, 205.1 kJ•mol^{-1} and 151.4 kJ•mol^{-1}, respectively.

Keywords   decomposition, 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5,5]undecane-3,9-dione, DSC, kinetics, TG

Introduction

2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5,5]udecane-3,9-dione is a typical cyclourea nitramine (Figure 1). Its crystal density is 1.91 g•cm^{-3}. The detonation velocity according to $\rho=1.90$ g•cm^{-3} is about 8670 m•s^{-1}. Its sensitivity to impact is better than that of cyclotrimethylenetrinitramine. So it is the potential high explosive. Its preparation,[1-3] properties,[1-3] hydrolytic behavior[4] and electronic structure[3] have been reported. In the present work, we report its kinetic parameters of the exothermic first-stage decomposition reaction with DSC and TG-DTG, which 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.
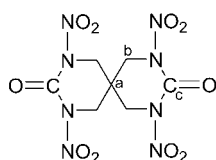

Figure 1 Structure of 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro-[5,5]udecane-3,9-dione.

Experimental

Material

2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5,5]udecane-

3,9-dione was prepared according to the reported method.[1-3] The compound was purified by recrystallyzation from acetone. ^{1}H NMR (solv. acetone, 90 MHz) δ: 4.60 (CH$_2$); ^{13}C NMR: δ: 35.63 (C-a), 53.55 (C-b), 146.42 (C-c); IR (KBr) v: 3040—2880, 1750, 1590, 1280 cm^{-1}; MS m/z: 272 (M$^+$−2NO$_2$), 181 (M$^+$−4NO$_2$). Anal. calcd for C$_7$H$_8$N$_8$O$_{10}$: C 23.08, H 2,22, N 30.79; found C 22.92, H 2.15, N 30.98. The sample was kept in a vacuum desiccator before use.

Experimental equipment and conditions

TG-DTG curve was obtained using a Perkin-Elmer model TGS-2 thermobalance. The heating rate was 10 ℃•min^{-1}. The flow rate of N$_2$ gas was 40 mL•min^{-1}. 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 under static air condition with five different heating rates ranging from 1 to 20 ℃•min^{-1}. DSC curves were obtained with a cell of aluminium (diameter 5 mm×3 mm), whose side was rolled up. α-Al$_2$O$_3$ was used as reference material. The sample was used about 0.7 mg. The calorimetric sensitivities were ±41.84 mJ•s^{-1}. The heating rate was calculated according to the actual rising rate of temperature from 50 ℃ to the temperature at the end of the reaction. The precision of temperature was 0.25 ℃. The temperature and heat

1076 *Chin. J. Chem.*, 2004, Vol. 22, No. 10

HU *et al.*

were calibrated using pure indium and tin powders as standard. DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of tests was satisfactory.

Results and discussion

Typical TG-DTG and DSC curves for the title compound are shown in Figures 2 and 3. DSC curve shows that only one exothermic peak. TG curve consisted of two-stage mass loss process without any stable intermediate product in which the first-stage began at about 234.6 ℃ and completed at 260.8 ℃ accompanied with 51.5 % mass loss.
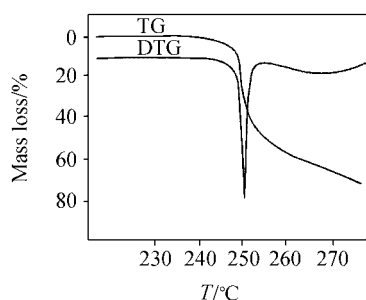
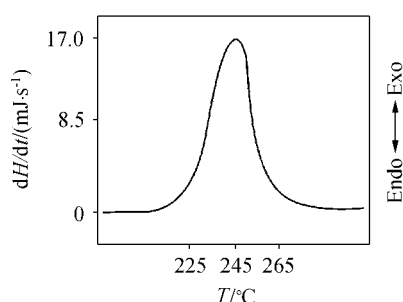**Figure 2** TG-DTG curve for the title compound at a heating rate of 10 ℃•min^{-1}.

Figure 3 DSC curve for the title compound at a heating rate of 5 ℃•min^{-1}.

In order to obtain the kinetic parameters (the apparent activation energy (E_a) and pre-exponential constant (A)) of the exothermic decomposition reaction for the title compound, a multiple heating method[5] (Kissinger's method) was employed. From the original data in Table 1, the apparent activation energy (E_k) is determined to be 205.1 kJ•mol^{-1}. The pre-exponential constant (A_k) is $10^{18.67}$ s^{-1}. The linear correlation coefficient (r_k) is

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

$\beta/(℃•min^{-1})$	$T_p/℃$
0.5194	218.75
1.059	227.90
2.156	234.75
5.192	243.75
10.42	248.35

0.9931. The value of E_o obtained by Ozawa's method[6] is 203.0 kJ•mol^{-1}. The value of r_o is 0.9936.

In order to obtain the values of E_a, A and the most probable kinetic model function from a single non-isothermal DSC curve, the integral Eq. (1),[7] differential Eq. (2)[7] and exothermic rate Eq. (3)[7] were employed.

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

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

$$\ln\left(\frac{dH_t}{dt}\right)_i=\ln\left\{AH_0\left\{f(\alpha)\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\right\}\right\}-\frac{E_a}{RT_i} \tag{3}$$

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model function, respectively, dH_t/dt is the exothermic heat flow at time t, H_0 is the total heat effect (corresponding to the global area under the DSC curve), H_t is the reaction heat at a certain time (corresponding to the partial area under the DSC curve), T_i is the temperature (K) at time t, α is the conversion degree ($\alpha=H_t/H_0$), T_0 is the initial point at which DSC curve deviates from the baseline, R is the gas constant, $\frac{d\alpha}{dT}=\frac{1}{H_0\beta}\frac{dH}{dt}$.

Forty-one types of kinetic model function in Ref. 8 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), standard mean square deviation (Q) and believable factor (d) ($d=Q(1-r)$) are obtained by the linear least-squares and iterative methods.[7] The values of E_a and A, corresponding to the probable kinetic model function (the mechanism function is No. 15) of the integral method selected by the minimal value of d (0.0000388) are 200.0 kJ•mol^{-1} and $10^{16.96}$ s^{-1}, respectively. The values of E_a and A, corresponding to the probable kinetic model function (the mechanism function is No.31) of the differential method selected by the minimal value of d (0.000266) are 250.0 kJ•mol^{-1} and $10^{23.75}$ s^{-1}, respectively. These values of E_a and A are not in the ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E_a=80$—250 kJ•mol^{-1} and log $A=7$—30 s^{-1}), belonging to reasonless kinetic parameters.

In order to obtain the reasonable kinetic parameters by the exothermic rate Eq. (3), we took the minimal values of the evaluation functions $\Omega(E, A, …)$

$$\Omega=\sum_{i=1}^{m}\left\{\ln\left(\frac{dH_t}{dt}\right)_i-\ln\left\{AH_0f(\alpha)\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\right\}+\frac{E_a}{RT_i}\right\} \tag{4}$$

Kinetics

Chin. J. Chem., 2004, Vol. 22, No. 10 **1077**

Once the value of E has been calculated from $\partial\Omega/\partial E=0$, the corresponding values of A, n, m and k in the forms of $f(\alpha)$ listed in Ref. 9 can then be obtained from the normal Eqs., $\partial\Omega/\partial A=0$, $\partial\Omega/\partial n=0$, $\partial\Omega/\partial m=0$ and $\partial\Omega/\partial k=0$. In the iterative computation process of combined dichotomous and least-squares methods, we took $AA=10^{-1}$, $BB=10^{10}$, $H=50.0$, $E_1=10^{-10}$ and $E_2=10^{-5}$, where E is the root of the Eq. $\partial\Omega/\partial E=0$, $[AA, BB]$ is the root interval of the Eq. $\partial\Omega/\partial E=0$, H is the step size, and E_1 and E_2 are two constants of the control precision. When the value of a certain point on the left side of the Eq. $\partial\Omega/\partial E=0$ is less than E_1 or half of the small interval length is less than E_2, this point or the intermediate point of the small interval is the solution of the Eq. $\partial\Omega/\partial E=0$. By substitution the original data in Table 2, and the fifteen form of $f(\alpha)$ in Ref. 9, into all the normal Eqs., the corresponding values of E of 216.4 kJ•mol^{-1} and A of $10^{20.51}$ s^{-1} and the probable empirical mechanism function of $\alpha^{0.122}(1-\alpha)^{0.528}$ are obtained by the method of logical choices.[7] These values of E_a and A obtained from a single non-isothermal DSC curve are in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. Therefore, it was concluded that the kinetic equation of thermal decomposition of the tile compound is

$$\frac{d\alpha}{dT}=10^{21.29}\alpha^{0.122}(1-\alpha)^{0.528}e^{-2.603\times10^4/T}$$

Table 2 Data of the title compound determined by DSC^a

Data point	T_i/K	α_i	$(dH_i/dt)_i/(mJ\cdot s^{-1})$	$d\alpha/dT\times10^3/K^{-1}$
1	472.2	0.0578	1.138	0.0154
2	473.2	0.0872	1.423	0.0192
3	474.2	0.0974	1.841	0.0249
4	475.2	0.1280	2.226	0.0301
5	476.2	0.1586	2.678	0.0362
6	477.2	0.1948	3.146	0.0426
7	478.2	0.2356	3.514	0.0476
8	479.2	0.3035	3.849	0.0521
9	480.2	0.3443	4.251	0.0575
10	481.2	0.3986	4.686	0.0634
11	482.2	0.4643	5.054	0.0684
12	483.2	0.5311	5.606	0.0759
13	484.2	0.6093	6.192	0.0838
14	485.2	0.6954	6.728	0.0911
15	486.2	0.7803	6.996	0.0947

^{a} $T_0=462.2$ K; $H_0=2216.7$ mJ; $\beta=2$ ℃•min^{-1}.

The value of E_a approached the dissociation energy of the N—NO$_2$ bond (229.9 kJ•mol^{-1}).[10]

The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta\rightarrow0$ obtained by Eq. (5) taken from Ref. 11 is 212.20 ℃.

$$T_{pi}=T_{p0}+b\beta_i+c\beta_i^2+d\beta_i^3, \quad i=1\text{—}5 \tag{5}$$

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (6) taken from Ref. 11 is 222.25 ℃.

$$T_b=\frac{E_o-\sqrt{E_o^2-4E_oRT_{p0}}}{2R} \tag{6}$$

where R is the gas constant (8.314 J•mol^{-1}•K^{-1}), E_o is the value of E obtained by Ozawa's method.

The entropy of activation ($\Delta^{\neq}S$), enthalpy of activation ($\Delta^{\neq}H$) and free energy of activation ($\Delta^{\neq}G$) corresponding to $T=T_{p0}$, $E=E_A$ and $A=A_k$ obtained by Eqs. (7), (8) and (9) are 108.3 J•mol^{-1}•K^{-1}, 205.1 kJ•mol^{-1} and 151.4 kJ•mol^{-1}, respectively.

$$A=\frac{k_BT}{h}e^{\Delta^{\neq}S/R} \tag{7}$$

$$A\exp\left(-\frac{E_a}{RT}\right)=\frac{k_BT}{h}\exp\left(\frac{\Delta^{\neq}S}{R}\right)\exp\left(-\frac{\Delta^{\neq}H}{RT}\right) \tag{8}$$

$$\Delta^{\neq}G=\Delta^{\neq}H-T\Delta^{\neq}S \tag{9}$$

where, k_B is the Boltzmann constant and h is the Planck constant.

Conclusion

The kinetic study on the exothermic first-stage decomposition reaction for the title compound was investigated. The empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of this reaction are $\alpha^{0.122}(1-\alpha)^{0.528}$, 216.4 kJ•mol^{-1} and $10^{20.51}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 222.25 ℃. The values of $\Delta^{\neq}S$, $\Delta^{\neq}H$ and $\Delta^{\neq}G$ of the reaction at T_{p0} are 108.3 J•mol^{-1}•K^{-1}, 205.1 kJ•mol^{-1} and 151.4 kJ•mol^{-1} respectively.

References

1 Willer, R. L. *U. S. A. AD-A 116832*, **1982**.

2 Willer, R. L. *J. Org. Chem.* **1984**, *49*, 5150.

3 Fu, Q.-J. ; Zhu, C.-H. *Acta Armamentarii* **1992**, *1*, 28.

4 Hu, R.-Z.; Liang, Y.-J.; Fang, Y.-G.; Wang, J.-S.; Xie, Y. *J. Therm. Anal.* **1996**, *46*, 1283.

5 Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.

6 Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881.

7 Hu, R.-Z.; Yang, Z.-Q.; Liang, Y.-J. *Thermochim. Acta* **1988**, *123*, 135.

8 He, S.-Y.; Liu, Y.; Zhao, J.-S.; Zhao, H.-A.; Yang, R.; Hu, R.-Z.; Shi, Q.-Z. *Chin. J. Chem.* **2003**, *21*, 139.

9 Hu, R.-Z.; Shi, Q.-Z. *Thermal Analysis Kinetics*, Science Press, Beijing, **2001**, p. 68 (in Chinese).

10 Cass, R. C.; Fletcher, S. E.; Mortimer, C. T.; Quincey, P. G.; Springall, H. D. *J. Chem. Soc.* **1958**, *3*, 958.

11 Zhang, T.-L.; Hu, R.-Z.; Xie, Y.; Li, F.-P. *Thermochim. Acta* **1994**, *244*, 171.

(E0403093 LI, W. H.)