Kinetic Study on the Exothermic Decomposition Reaction of 2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]onan-3,7-dione

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The kinetic parameters of the exothermic decomposition reaction of the title compound in a temperature-programmed mode have been studied by means of DSC. The empirical kinetic model function in differential form, apparent activation energy (E_a) and pre-exponential factor (A) of this reaction are $(1-\alpha)^{0.222}$, 225.8 kJ•mol^{-1} and $10^{20.21}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 224.9 ℃.

Keywords   decomposition, 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]nonan-3,7-dione, kinetics

Introduction

2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]nonan-3,7-dione (**1**) is a novel energetic cyclourea nitramine containing four —NO$_2$ groups (Figure 1). The detonation velocity corresponding to $\rho=1.93$ g•cm^{-3} is 9034 m•s^{-1}. It is the potential high explosive. Its preparation,[1] properties[1] and hydrolytic behavior[2] have been reported. Thermal behavior is one of the most important aspects of the compound in practical application. However, its kinetic parameters of thermal decomposition have not yet been reported. The aim of this work is to study the kinetic parameters of the exothermic decomposition reaction of the compound by DSC. These data are quite useful in the evaluation of its thermal stability under non-isothermal condition and in the study on its thermal changes at high temperature.
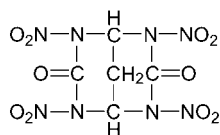

Figure 1   General structure of 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]nonan-3,7-dione (**1**).

Experimental

2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]nonan-3,7-dione was prepared according to the reported method.[1] The compound **1** was purified by recrystal-

lyzation from nitromethane. ^{1}H NMR (solv. acetone, 90 MHz) δ: 7.87 (t, $J>$CHCH$_2$=3 Hz, $>$CH—, 2H), 3.62 (t, —CH$_2$—, 2H); IR (KBr) v: 2990 ($>$C=O), 1790 ($>$C=O), 1630, 1295 (N—NO$_2$) cm^{-1}. Anal. calcd for C$_5$H$_4$N$_8$O$_{10}$: C 17.84, H 1.19, N 33.33; found C 18.02, H 1.17, N 33.77. The sample was kept in a vacuum desiccator before use.

DSC experiments were carried out with a CDR-1 thermal analyzer made in Shanghai Balance Instrument Factory, using Ni/Cr-Ni/Si thermocouple plate working in static air with heating rates 1—20 ℃•min^{-1}. α-Al$_2$O$_3$ was used as reference material. The DSC curves were obtained with a cell of aluminium (diameter 5 mm× 3 mm), whose side was rolled up. The heating rate was calculated according to the actual rate of temperature rising from 50 ℃ to the temperature at the end of the decomposition. The sample was used about 0.7 mg. DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of tests was satisfactory.

Analysis of kinetic data

Typical DSC curve of compound **1** is shown in Figure 2, which shows only one exothermic peak. In order to obtain the kinetic parameters (the apparent activation energy (E_a) and pre-exponential constant (A)) of the exothermic decomposition reaction, a multiple heating method[3] (Kissinger's method) was employed. From the original data in Table 1, E_a is determined to be 222.0 kJ•mol^{-1} and A is $10^{20.53}$ s^{-1}. The linear correlation coefficient (r_k) is 0.9993. The value of E_a and the linear

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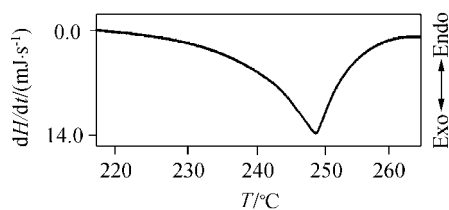
Figure 2 DSC curve of the thermal decomposition of compound **1** at a heating rate of 5 ℃•min^{-1}.

Table 1 The 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})	T_p/℃
0.500	218
1.053	225
2.074	233
5.167	242
10.50	247
21.43	252

correlation coefficient (r_o) obtained by Ozawa's method[4] are 219.1 kJ•mol^{-1} and 0.9943, respectively.

The integral Eq. (1), differential Eq. (2) and exothermic rate Eq. (3) 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]

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

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

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

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 is the gas constant, 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 ($\alpha = H_t/H_0$), $\frac{d\alpha}{dT} = \frac{1}{H_0\beta}\frac{dH}{dt}$.

Thirty types of kinetic model function[6] and the data in Table 2 are put into Eqs. (1) and (2), respectively. The values of E_a, A, linear correlation coefficient (r) and standard mean square deviation (Q) are obtained by the

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})	$d\alpha/dT \times 10^3$/K^{-1}
1	494.85	0.02586	0.95395	5.969
2	497.35	0.04485	1.4518	9.085
3	499.85	0.07246	2.0962	13.12
4	501.85	0.10252	2.7405	17.15
5	503.35	0.13084	3.3388	20.89
6	504.85	0.16536	4.0250	25.18
7	506.35	0.20709	4.9580	31.02
8	507.65	0.24863	5.6777	35.52
9	508.65	0.28709	6.5731	41.13
10	509.65	0.33083	7.4768	46.78
11	510.85	0.39360	8.6567	54.17
12	511.85	0.45081	9.6525	60.40
13	512.65	0.49795	10.079	63.07
14	513.35	0.54869	11.213	70.16
15	514.15	0.60285	11.824	73.99
16	514.85	0.66022	12.477	78.07
17	515.85	0.74102	13.259	82.97
18	516.85	0.82516	13.569	84.90

[a] T_0=484.85 K; H_0=1917.7 mJ; β=5.0 ℃•min^{-1}.

linear least-squares and iterative methods.[5]

The probable kinetic model functions of the integral and differential methods selected by the better value of r and Q, 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 listed in Table 3. Their general expression is $f(\alpha)=(1-\alpha)^n$. Substituting $f(\alpha)=(1-\alpha)^n$ into Eq. (3) and taking logarithm on both sides of Eq. (3), the following relation is obtained

$$\ln\left(\frac{dH_t}{dt}\right)_i = \ln\left\{AH_0\left\{(1-\alpha_i)^n\left[1 + \frac{E_a}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right]\right\}\right\} - \frac{E_a}{RT_i}$$

then the mean-square procedure is applied by taking minimal values of evaluation functions (E_a, A and n)

$$\Omega = \sum_{i=1}^m\left\{\ln\left(\frac{dH_t}{dt}\right) - \ln\left\{AH_0(1-\alpha_i)^n\left[1 + \frac{E_a}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right]\right\} + \frac{E_a}{RT_i}\right\}^2 \tag{4}$$

Eq. (4) is satisfied under condition that

$\partial\Omega/\partial A = 0$ (5)

$\partial\Omega/\partial n = 0$ (6)

$\partial\Omega/\partial E_a = 0$ (7)

or

Table 3 Kinetic parameters obtained by the data in Table 2

Equation	$f(\alpha)$	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\log A$ (A in s^{-1})	r	Q
(1)	$2(1-\alpha)^{1/2}$	248.8	22.30	0.9995	0.0104
	$(1-\alpha)^{0}$	220.1	19.60	0.9991	0.0138
	$\dfrac{1}{2}(1-\alpha)^{-2}$	172.4	14.90	0.9862	0.1341
(2)	$(1-\alpha)^{0}$	198.2	17.36	0.9953	0.0589
(3)	$(1-\alpha)^{0.222}$	225.8	20.21	—	0.0040

$$m \ln A + an = b + \frac{E_\text{a}}{R}c - m \ln H_0 - d \tag{8}$$

$$a \ln A + en = f + \frac{E_\text{a}}{R}g - a \ln H_0 - h \tag{9}$$

$$p - (\ln A + \ln H_0)q - nr - s + \frac{E_\text{a}}{R}W = 0 \tag{10}$$

where

$$a = \sum_{i=1}^{m} \ln(1-\alpha_i) \tag{11}$$

$$b = \sum_{i=1}^{m} \ln\left(\frac{dH_\text{t}}{dt}\right)_i \tag{12}$$

$$c = \sum_{i=1}^{m} \frac{1}{T_i} \tag{13}$$

$$d = \sum_{i=1}^{m} \ln\left[1 + \frac{E_\text{a}}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right] \tag{14}$$

$$e = \sum_{i=1}^{m} \ln^2(1-\alpha_i) \tag{15}$$

$$f = \sum_{i=1}^{m} \ln\left(\frac{dH_\text{t}}{dt}\right)_i \ln(1-\alpha_i) \tag{16}$$

$$g = \sum_{i=1}^{m} \frac{\ln(1-\alpha_i)}{T_i} \tag{17}$$

$$h = \sum_{i=1}^{m} \left\{ \ln\left[1 + \frac{E_\text{a}}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right] \cdot \ln(1-\alpha_i) \right\} \tag{18}$$

$$Q_i = \frac{1}{RT_i} - \frac{1 - \dfrac{T_0}{T_i}}{RT_i + E_\text{a}\left(1 - \dfrac{T_0}{T_i}\right)} \tag{19}$$

$$p = \sum_{i=1}^{m} Q_i \ln\left(\frac{dH_\text{t}}{dt}\right)_i \tag{20}$$

$$q = \sum_{i=1}^{m} Q_i \tag{21}$$

$$r = \sum_{i=1}^{m} Q_i \ln(1-\alpha_i) \tag{22}$$

$$s = \sum_{i=1}^{m} Q_i \ln\left[1 + \frac{E_\text{a}}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right] \tag{23}$$

$$W = \sum_{i=1}^{m} \frac{Q_i}{T_i} \tag{24}$$

Solving Eqs. (8) and (9), we obtained

$$\ln A = \frac{(b-d)e + (h-f)a + \dfrac{E_\text{a}}{R}(ce-ga)}{-(a^2-me)} - \ln H_0 \tag{25}$$

and

$$n = \frac{(b-d)a + (h-f)m + \dfrac{E_\text{a}}{R}(ac-gm)}{a^2-me} \tag{26}$$

The values of p, $\ln A$, q, n, r, s and W in Eq. (10) are correlated with the value of E_a. Once the value of E_a has been calculated from Eq. (10), the corresponding values of A and n can be obtained from Eqs. (25) and (26).

By substituting the original data tabulated in Table 2 into above-mentioned Eqs. (11)—(24), the value of E_a of 225.8 kJ·mol^{-1} was obtained by Eq. (10) and the values of A of $10^{20.21}$ s^{-1} and n of 0.222 were obtained by Eqs. (25) and (26) respectively. The values of E_a and A obtained by Eq. (4) 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 the exothermic decomposition reaction is

$$\frac{d\alpha}{dT} = 10^{21.29}(1-\alpha)^{0.222}\,e^{-2.716 \times 10^4 /T}$$

The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \to 0$ obtained by Eq. (27) taken from Ref. 7 is 215.5 ℃.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1\text{—}6 \tag{27}$$

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (28) taken from Ref. 7 is 224.9 ℃.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_o R T_{p0}}}{2R} \tag{28}$$

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.

Conclusion

The empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of the exothermic decomposition reaction for the title compound are $(1-\alpha)^{0.222}$, 225.8 kJ•mol^{-1} and $10^{20.21}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 224.9 ℃.

References

1 Hong, G.-L.; Zhu, C.-H. *Synthesis and Properties of Tetranitropropanediurea*. In *Proceedings of the 17th International Pyrotechnics Seminar combined with the 2nd Beijing International Symposium on Pyrotechnics and Explosives*, Eds: Ou, Y.-X.; Feng, G.-C.; Zhang, B.-P., Beijing Institute of Technology Press, Beijing, **1991**, p. 193.

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

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 Hu, R.-Z.; Yang, D.-S.; Gao, S.-L.; Chen, S.-P.; Zhao, H.-A.; Shi, Q.-Z. *J. Hazard. Mater.* **2003**, *A102*, 147.

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