Kinetics and Mechanism of the Exothermic First-stage Decomposition Reaction for 1,5-Dimethyl-2,6-bis(2,2,2-trinitroethyl)-glycoluril

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The thermal behavior, mechanism and kinetic parameters of the exothermic first-stage decomposition reaction of the title compound in a temperature-programmed mode have been investigated by means of DSC, TG-DTG and IR. The reaction mechanism was proposed. The empirical kinetic model functions in differential form, apparent activation energy (E_a) and pre-exponential factor (A) of this reaction are $(1-\alpha)^{-1.119}$, 211.3 kJ/mol and $10^{20.2}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 202.2 ℃. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of this reaction are 143.8 $J\cdot mol^{-1}\cdot K^{-1}$, 208.7 kJ/mol and 141.7 kJ/mol, respectively.

Keywords decomposition, glycoluril, kinetics, mechanism

Introduction

Cyclourea nitramines with *N*-trinitroethyl groups have a greater density and a higher detonation velocity. Some of the compounds could be used as high explosives. 1,5-Dimethyl-2,6-bis(2,2,2-trinitroethyl)glycoluril (**1**) is a typical cyclourea nitramine. The crystal density is 1.74 g/cm^3 and the detonation velocity corresponding to $\rho = 1.74$ g/cm^3 is about 8066 m/s. Therefore, it is very possible that the compound is used as high explosive. Its hydrolytic behavior[1] has been reported. In this paper, its kinetic parameters and mechanism of the exothermic first-stage 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.

Experimental

1,5-Dimethyl-2,6-bis(2,2,2-trinitroethyl)glycoluril (**1**) was prepared in our institute. Its purity is more than 99.5%. The sample was kept in a vacuum desiccator.

TG-DTG curve was obtained using a Perkin-Elmer Model TGS-2 thermobalance. The heating rate was 10 ℃/min. The flow rate of N_2 gas was 40 mL/min. DSC experiments were carried out with 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. α-Al_2O_3 was used as reference material. The infrared spectra of solid intermediate products were recorded on a Perkin Elmer Model 180 IR spectrophotometer. The gaseous intermediate products of the TG experiments were blown under high-purity N_2 gas and absorbed in an acetic acid solution of α-naphthylamine and *p*-aminobenzenearsonic acid. This solution, containing nitrogen dioxide, was purplish-red in appearance.

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Results and discussion

Thermal behavior and decomposition mechanism

Typical TG-DTG and DSC curves for compound **1** are shown in Figs. 1 and 2. DSC curve shows only one exothermic peak, while TG curve shows two-stage mass loss without any stable intermediate product formed in which the first stage began at about 172 ℃ and completed at 235 ℃ accompanied with 66% mass loss. It is in agreement with the theoretical value of the mass loss of 66%, corresponding to the loss of two-trinitroethyl group attached to nitrogen atom on two sides of carbonyl to obtain 1,5-dimethyl-glycoluril.

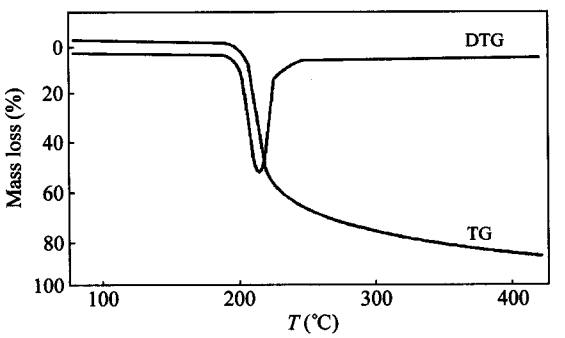


Fig. 1 TG-DTG curve for compound **1** at a heating rate of 10 ℃/min.

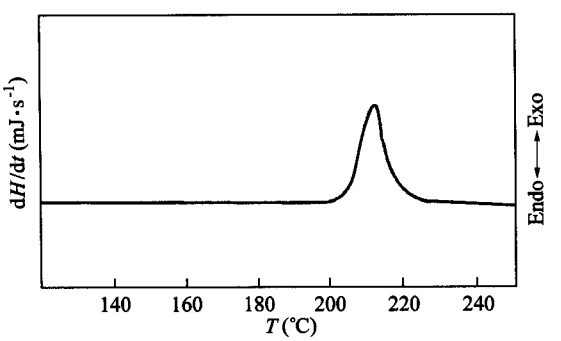
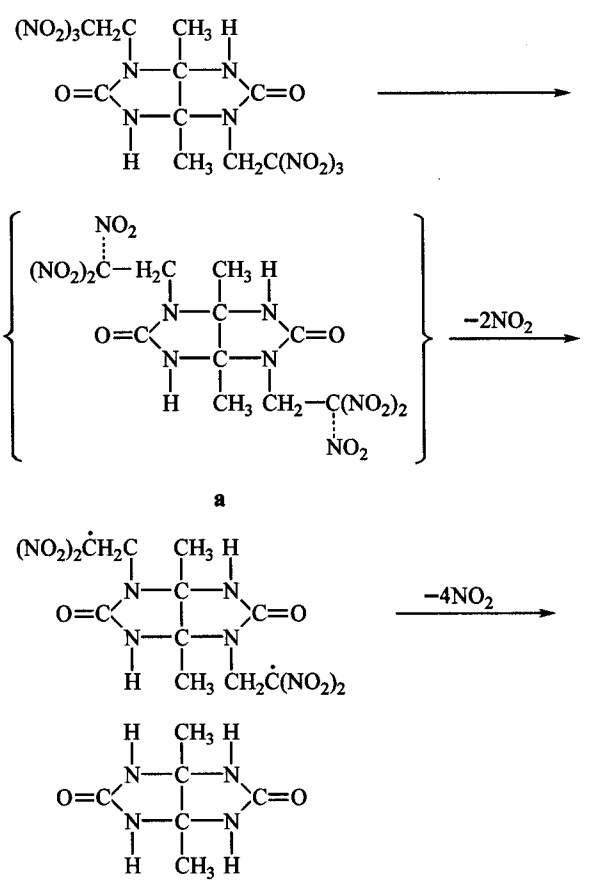


Fig. 2 DSC curve for compound **1** at a heating rate of 5 ℃/min.

In order to understand the first-stage decomposition process of compound **1**, decomposition-interruption tests were conducted with DSC experiments. Thermal degradation of compound **1** was performed by heating the sample to a certain temperature in the first-stage decomposition and then cooling down to the room temperature. The infrared analyses of compound **1** before thermal decomposition and intermediate product after above-mentioned decomposion-interuption tests were conducted. By the end of the first-stage, the characteristic absorption peaks for trinitroethyl group of compound **1** disappear at 1600 and 1300 cm^{-1}. However the characteristic absorption peak for the N—H group is at 3240 cm^{-1} and those of the C—N group are at 1160 and 1050 cm^{-1}. The characteristic absorption peaks of the CH_3 group at 2930, 2860 and 1435 cm^{-1} do not disappear. The characteristic absorption peaks of C = O widen. These observations show that the parent ring of compound **1** indeed exists. The absorbed solution containing the gaseous intermediate product is purplish-red in appearance, indicating that nitrogen dioxide gas is liberated at the beginning of the decomposition of compound **1**.

On the basis of the above-mentioned experiments and the calculated result, the mechanism of the exothermic first-stage decomposition reaction for compound **1** could be shown as Scheme 1.

Scheme 1



Analysis of kinetic data

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the exothermic first-stage decomposition reaction for compound **1**, a multiple heating method[2] (Kissinger's method) was employed. From the original data in Table 1, E_a is determined to be 208.7 kJ/mol and A $10^{20.5}$ s^{-1}. The linear correlation coefficient (r_K) is 0.9969. The values of E_a and r_o obtained by Ozawa's method[3] are 206.1 kJ/mol and 0.9971, respectively.

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

β (℃/min)	1.156	2.000	5.250	10.60	22.75
T_p (℃)	197.5	203.5	211.2	218.8	224.0

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.[4]

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

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

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

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model function, respectively, T_0 the initial point at which DSC curve deviates from the baseline, R the gas constant, 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_i the temperature (K) at time t, α the conversion degree ($\alpha = H_t/H_0$), $\frac{d\alpha}{dT}=\frac{1}{H_0\beta}\frac{dH}{dt}$.

Forty-one types of kinetic model function[5] 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) (where $d = Q/r$) are obtained by the linear least-squares and iterative methods.[4]

The probable kinetic model functions of the integral and differential methods selected by the minimal value of d and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials (E = 80—250 kJ/mol, log A = 7—30 s^{-1}, $r > 0.99$ and $Q < 0.1$) are $f(\alpha)=\frac{1}{2}(1-\alpha)^{-1}$ and $f(\alpha)=\frac{1}{3}(1-\alpha)^{-2}$, respectively. 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)

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

Eq. (4) is satisfied under condition that

$$\begin{cases}\partial\Omega/\partial A=0 & (5)\\ \partial\Omega/\partial n=0 & (6)\\ \partial\Omega/\partial E_a=0 & (7)\end{cases}$$

or

$$\begin{cases}m\ln A+an=b+\frac{E_a}{R}c-m\ln H_0-d & (8)\\ a\ln A+en=f+\frac{E_a}{R}g-a\ln H_0-h & (9)\\ p-(\ln A+\ln H_0)g-nr-s+\frac{E_a}{R}W=0 & (10)\end{cases}$$

where

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

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

$$c = \sum_{i=1}^{m} \frac{1}{T_i} \quad (13)$$

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

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

$$f = \sum_{i=1}^{m} \ln\left(\frac{dH_t}{dt}\right)_i \ln(1 - \alpha_i) \quad (16)$$

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

$$h = \sum_{i=1}^{m} \left\{\ln\left[1 + \frac{E_a}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right]\ln(1 - \alpha_i)\right\} \quad (18)$$

$$Q_i = \frac{1}{RT_i} - \frac{1 - \frac{T_0}{T_i}}{RT_i + E_a\left(1 - \frac{T_0}{T_i}\right)} \quad (19)$$

$$p = \sum_{i=1}^{m} Q_i \ln\left(\frac{dH_t}{d_t}\right)_i \quad (20)$$

$$q = \sum_{i=1}^{m} Q_i \quad (21)$$

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

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

$$W = \sum_{i=1}^{m} \frac{Q_i}{T_i} \quad (24)$$

Solving Eqs. (8) and (9), it could be obtained

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

and

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

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 211.3 kJ/mol is obtained by Eq. (10), and the values of A of $10^{20.2}$ s^{-1} and n of -1.119 are obtained by Eqs. (25) and (26), respectively. The kinetic parameters obtained by the data in Table 2 are summarized in Table 3. The values of E_a and A obtained by Eq. (4) are in good agreement with the calculated values by Kissinger's method and Ozawa's method. The value of E_a approached the dissociation energy of the C—NO_2 bond, indicating that the activated complex **a** as shown in Scheme 1 could be formed during the decomposition.

The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (27) taken from Ref. [6] is 193.1 ℃.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1,2,3,4,5 \quad (27)$$

Table 2 Data of compound **1** determined by DSC[a]

Data point	T_i (K)	α_i	$(dH_i/dt)_i$ (mJ/s)
1	470.15	0.0419	0.9707
2	471.65	0.0637	1.251
3	472.65	0.0826	1.577
4	473.65	0.1059	1.925
5	474.65	0.1349	2.431
6	475.35	0.1612	2.720
7	476.15	0.1921	3.226
8	476.85	0.2283	3.770
9	477.35	0.2556	4.092
10	477.85	0.2856	4.510
11	478.35	0.3187	4.954
12	478.85	0.3558	5.661
13	479.35	0.3990	6.740
14	479.85	0.4535	8.339
15	480.15	0.4880	10.31
16	480.35	0.5278	11.13
17	480.65	0.5704	11.78

[a] $T_0 = 461.65$ K; $H_0 = 820.4$ mJ; $\beta = 0.08333$ ℃/s.

Table 3 Kinetic parameters obtained by the data in Table 2

No.	Equation	$f(\alpha)$	E (kJ/mol)	log (A/s^{-1})	R	Q	D
1	(1)	$\frac{1}{3}(1-\alpha)^{-2}$	215.5	19.3	0.9926	0.0326	0.0002
2	(2)	$\frac{1}{2}(1-\alpha)^{-1}$	225.2	22.1	0.9933	0.0325	0.0002
3	(3)	$(1-\alpha)^{-1.119}$	211.3	20.2	—	0.0300	—

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (28) taken from Ref. [6] is 202.2 ℃.

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{p0}}}{2R} \quad (28)$$

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 $T = T_{p0}$, $E = E_k$ and $A = A_k$ obtained by Eqs. (29), (30) and (31) are 143.8 J·mol^{-1}·K^{-1}, 208.7 kJ/mol and 141.7 kJ/mol, respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^{\neq}/R} \quad (29)$$

$$A\exp(-E/RT) = \frac{k_B T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \quad (30)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (31)$$

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

Conclusions

The mechanism of the exothermic first-stage decomposition reaction for the title compound **1** could be expressed as Scheme 1. The empirical kinetic model function in differential form, apparent activation energy and pre-exponential factor of this reaction are $(1-\alpha)^{-1.119}$, 211.3 kJ/mol and $10^{20.2}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 202.2 ℃. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of the reaction at T_{p0} are 143.8 J·mol^{-1}·K^{-1}, 208.7 kJ/mol and 141.7 kJ/mol, respectively.

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