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Kinetics and mechanism of the exothermic first-stage decomposition reaction for 1,5-dimethyl-2,6-bis(2,2,2-trinitroethyl)-4,8-dinitroglycoluril

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Abstract

Under linear temperature increase condition the thermal behavior, mechanism and kinetic parameters of the exothermic first-stage decomposition reaction of the title compound have been studied by means of DSC, TG–DTG and IR. The reaction mechanism was proposed.

The kinetic model function in differential form, apparent activation energy and pre-exponential constant of this reaction are $(1-\alpha)^{0.5}$, 194.7 kJ mol^{-1} and $10^{18.45}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 200.8 °C. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of this reaction are 133.3 J mol^{-1} K^{-1}, 203.9 kJ mol^{-1} and 142.0 kJ mol^{-1}, respectively.

Keywords: Decomposition; 1,4-Dinitro-3,6-bis(trinitroethyl)glycoluril; DSC; Kinetics; Mechanism; TG

1. 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)-4,8-dinitroglycoluril is a typical cyclourea nitramine. Its crystal density is 1.84 g cm^{-3}. The detonation velocity corresponding to $\rho = 1.84$ g cm^{-3} is about 8773 m s^{-1}. It has the potential for possible use as high explosive from the point of view of the above-mentioned high performance. Its preparation [1] and properties [1] have been reported. In the present work, we report its kinetic parameters and mechanism of the exothermic first-stage decomposition reaction studied with DSC, TG–DTG and IR. 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.

2. Experimental

2.1. Materials

The purified 1,5-dimethyl-2,6-bis(2,2,2-trinitroethyl)-4,8-dinitroglycoluril was prepared by our institute. Its purity was more than 99.5%. Sample was kept in a vacuum desiccator.

2.2. Experimental

TG–DTG curve was obtained using a Perkin-Elmer Model TGS-2 thermobalance. The heating rate was 10 °C min^{-1}. The flow rate of N_2 gas was 40 ml/min. DSC experiments were carried out with MODEL CDR-1 thermal analyzer made in the 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 °C min^{-1}. The α-Al_2O_3 was used as reference material in the DSC measurements. The infrared spectra of solid intermediate products were recorded using a Perkin Elmer Model 180 IR spectrophotometer. The gaseous intermediate products of the TG experiments were blown with 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.

3. Results and discussion

3.1. Thermal behavior and decomposition mechanism

Typical TG–DTG and DSC curves for the title compound are shown in Figs. 1 and 2. The appearance of two peaks

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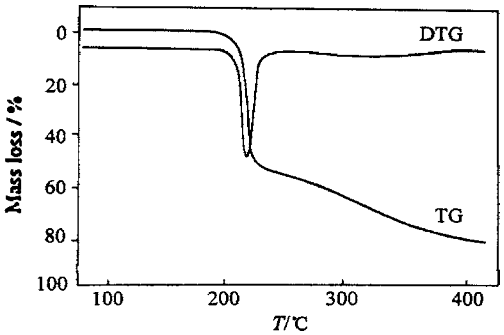


Fig. 1. TG–DTG curve for the title compound at a heating rate of $10\,\mathrm{min}^{-1}$.

in the DSC curve suggested that the thermal decomposition process of the title compound occurs in two steps. The TG curve consisted also of two-stage mass loss process.

The first-stage began at about 170 °C and completed at 240 °C accompanied with 56% mass loss. It is in agreement with the theoretical value of the mass loss of 55.7%, corresponding to the loss of two trinitroethyl group attached to nitrogen atom on two sides of carbonyl to obtain 1,5-dimethyl-4,8-dinitroglycoluril. In order to understand the first-stage decomposition process of the title compound, decomposition-interruption tests were conducted with DSC experiments. Thermal degradation of the title compound 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 the title compound before and after thermal decomposition were conducted. By the end of the first-stage, the characteristic absorption peaks for trinitroethyl group of the title compound disappeared at 1600 and $1300\,\mathrm{cm}^{-1}$. However, the characteristic absorption peaks for the N–NO_2 group at 1580 and $1270\,\mathrm{cm}^{-1}$ and the –CH_3 group at 2930, 2860 and $1435\,\mathrm{cm}^{-1}$ did not disappear. The characteristic absorption peaks of > C=O widen. These observations show that the parent ring of title compound did indeed exist. The absorbed solution, containing the gaseous intermediate product was purplish red in appearance, indicating that nitrogen dioxide gas was liberated at the beginning of the decomposition of the title compound.

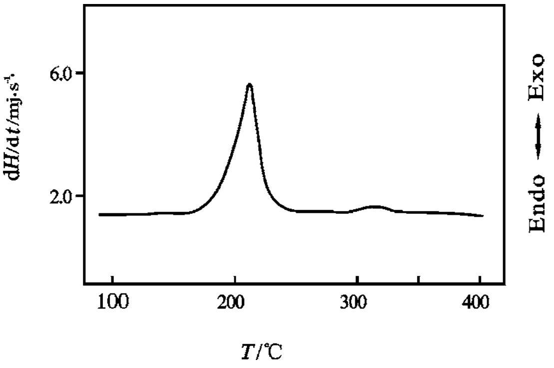
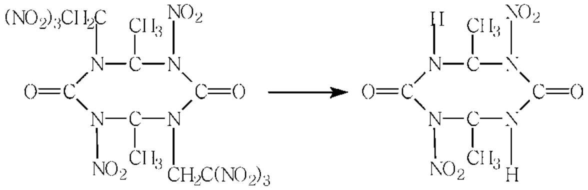


Fig. 2. DSC curve for the title compound at a heating rate of $5\,^{\circ}\mathrm{C\,min}^{-1}$.

On the basis of above-mentioned experiments and calculated result, the mechanism of the exothermic first-stage decomposition reaction for the title compound could be expressed by the following scheme:



3.2. Analysis of kinetic data

In order to obtain the kinetic parameters (the apparent activation energy (E_a) and pre-exponential constant (A)) of the exothermic first-stage decomposition reaction for the title compound, a multiple heating method [2] (Kissinger's method) was employed. From the original data in Table 1, the apparent activation energy (E_k) is determined to be $203.9\,\mathrm{kJ\,mol}^{-1}$. The pre-exponential constant (A_k) is $10^{19.95}\,\mathrm{s}^{-1}$. The linear correlation coefficient (r_k) and variance (Q) is 0.9950 and 0.0560, respectively. The value of E_o obtained by Ozawa's method [3] is $201.5\,\mathrm{kJ\,mol}^{-1}$. The value of r_0 and Q is 0.9954 and 0.0106, respectively.

In order to obtain the values of E_a, A and reaction order (n) from a single non-isothermal DSC curve, the integral rate equation (1) [4] and differential equation (2) [4] were employed:

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

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

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model functions, respectively, $\mathrm{d}\alpha/\mathrm{d}T=(1/H_0\beta)(\mathrm{d}H/\mathrm{d}t)$, $\mathrm{d}H/\mathrm{d}t$ 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, α the conversion degree ($\alpha=H_t/H_0$), T_0 the initial point at which DSC curve deviates from the baseline, and R the gas constant.

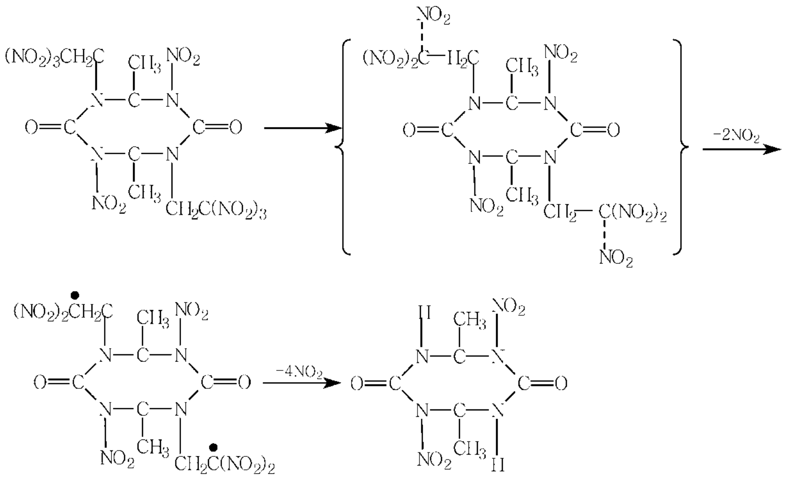
Table 1
The maximum peak temperature (T_p) of the exothermic first-stage decomposition reaction for the title compound determined by the DSC curves at various heating rates (β)

β ($^{\circ}\mathrm{C\,min}^{-1}$)	T_p (°C)
1.146	196.5
1.906	203.5
5.188	211.5
11.13	217.2
23.00	225.2

Forty-one types of kinetic model functions in Ref. [5] and the original data tabulated in Table 2 are put into Eqs. (1) and (2). The probable kinetic model function selected by the minimal value of d and the values of E_a, A, linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d, where $d = Q/r$) obtained by Eq. (1) with the linear least-squares method [4] (program IM) on the computer are $f(\alpha) = (1-\alpha)^{0.5}$, $G(\alpha) = 2[1-(1-\alpha)^{0.5}]$, 191.1 kJ mol^{-1}, $10^{16.3}$ s^{-1}, 0.9992, 0.0095, and 7.5×10^{-6}, respectively. The values of E_a, A, r, Q and d obtained by Eq. (2) with iterative method [4] (program DM) on the computer, which corresponds to $f(\alpha) = (1-\alpha)^{0.5}$ are 194.7 kJ mol^{-1}, $10^{18.5}$ s^{-1}, 0.9893, 0.1359 and 1.5×10^{-3}, respectively. Their values of E are very close to each other. Therefore, we conclude that the kinetic equation of exothermic first-stage decomposition reaction of the title compound is

$$\frac{d\alpha}{dT} = \left\{\frac{A}{\beta}\left[1 + \frac{E}{RT}\left(1 - \frac{E}{RT}\right)\right] \exp\left(-\frac{E}{RT}\right)\right\}(1-\alpha)^{0.5}$$

The 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. The value of E_a approached the dissociation energy of the C–NO$_2$ bond, indicating that the activated complex (**a**) as shown in the following scheme could be formed during decomposition:



The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \to 0$ obtained by Eq. (26) of [6] is 191.51 °C:

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

where b, c and d are coefficients: $b = 6.16786$, $c = -0.48181$, and $d = 0.01206$.

The critical temperature of thermal explosion (T_b) obtained from Eq. (4) of [6] is 200.8 °C:

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

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

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})
1	461.65	0.0436	0.7029
2	463.65	0.0632	0.9540
3	465.65	0.0892	1.234
4	467.15	0.1137	1.473
5	468.65	0.1418	1.665
6	470.15	0.1738	1.862
7	471.65	0.2104	2.151
8	473.15	0.2530	2.519
9	474.15	0.2856	2.841
10	474.65	0.3033	3.008
11	475.35	0.3320	3.305
12	476.15	0.3637	3.665
13	476.85	0.3988	4.063
14	477.65	0.4375	4.481
15	478.35	0.4802	4.920
16	479.15	0.5268	5.293
17	479.85	0.5768	5.678
18	480.65	0.6292	5.832

[a] $T_0 = 447.15$ K; $H_0 = 988.85$ mJ; $\beta = 0.08333$ °C s^{-1}.

The entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) corresponding to $T = T_{p0}$, $E = E_k$ and $A = A_k$ obtained by Eqs. (28)–(30) are 133.3 J mol^{-1} K^{-1}, 203.9 kJ mol^{-1} and 142.0 kJ mol^{-1}, respectively:

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

$$A \exp\left(-\frac{E_a}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{6}$$

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

where k_B is the Boltzmann's constant and h the Planck's constant.

4. Conclusions

The mechanism of the exothermic first-stage decomposition reaction for the title compound could be expressed by the scheme shown in the text. The apparent activation energy, pre-exponential constant and reaction order of this reaction are 194.7 kJ mol^{-1}, $10^{18.45}$ s^{-1} and 0.5, respectively. The critical temperature of thermal explosion of the compound is 200.8 °C. The values of $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ of the reaction at T_{p0} are 133.3 J mol^{-1} K^{-1}, 203.9 kJ mol^{-1} and 142.0 kJ mol^{-1}, respectively.

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