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Kinetics and mechanism of the exothermic first-stage decomposition reaction for 1,4-dinitro-3,6-bis(trinitroethyl) glycoluril

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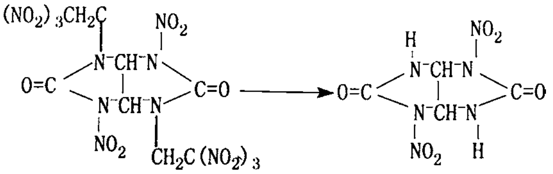
Abstract

Under linear temperature increase condition the thermal behaviour, 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 could be expressed by the following



. The apparent activation energy, pre-exponential constant and reaction order of this reaction are 203.1 kJ mol^{-1}, $10^{19.9}$ s^{-1} and 0, respectively. The critical temperature of thermal explosion of the compound is 191.4 °C. The values of $\Delta S^{\neq}$ $\Delta H^{\neq}$ and $\Delta G^{\neq}$of this reaction are 132.5 J mol^{-1}, 199.09 and 138.74 kJ mol^{-1}, respectively. © 2002 Elsevier Science B.V. All rights reserved.

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

1. Introduction

1,4-Dinitro-3,6-bis(trinitroethyl) glycoluril is a typical cyclourea nitramine. Its crystal density is 1.95 g cm^{-3}. The detonation velocity corresponding to $\rho = 1.897$ g cm^{-3} is about 9037 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], properties [1] and hydrolytic behaviour [2] 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.

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2. Experimental

2.1. Materials

The purified 1,4-dinitro-3,6-bis(trinitroethyl) glycoluril 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^{-1}. 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 behaviour 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 in the DSC and DTG curves 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 180 °C and completed at 230 °C accompanied with 55% mass loss. It is in agreement with the theoretical value of the mass loss of 58%, corresponding to the loss of two trinitroethyl group attached to nitrogen atom on two sides of carbonyl to obtain 1,4-dinitro-glycoluril. 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.

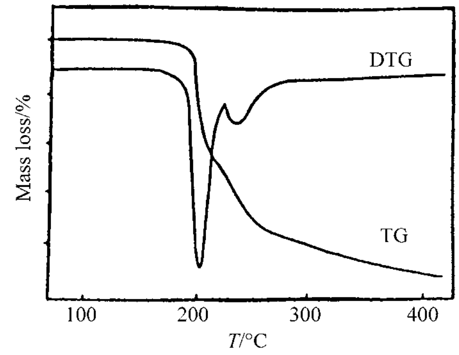


Fig. 1. TG-DTG curve for the title compound at a heating rate of 10 °C min^{-1}.

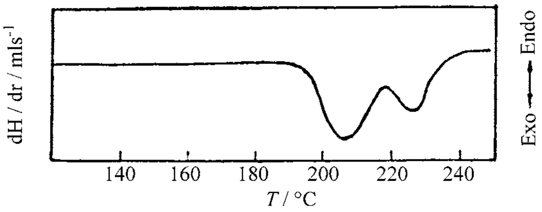


Fig. 2. DSC curve for the title compound at a heating rate of 5 °C min^{-1}.

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 1610 and 1300 cm^{-1}. However, the characteristic absorption peaks for the N–NO_2 group at 1585 and 1275 cm^{-1} and the –CH group at 3020, 1440 and 1380 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.

On the basis of above-mentioned experiments and calculated result, the mechanism of the exothermic

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 (°C min^{-1})	T_p (°C)
1.0417	188
2.1429	192
5.4838	203
10.968	209
22.480	214

first-stage decomposition reaction for the title compound could be expressed by the reaction mechanism shown in the abstract.

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 [3] (Kissinger's method) was employed. From the original data in Table 1, the apparent activation energy (E_a) is determined to be 199.1 kJ mol^{-1}. The pre-exponential constant (A) is $10^{19.9}$ s^{-1}. The linear correlation coefficient (r_K) is 0.9937.The value of E_a obtained by Ozawa's method [4] is 196.8 kJ mol^{-1}. The value of r_0 is 0.9942.

In order to obtain the values of E_a, A and reaction order (n) from a single non-isothermal DSC curve, the exothermic rate Eq. (1) [5] and differential Eq. (2) [5] were employed.

$$\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i = AH_0\left\{(1-\alpha_i)^n\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\right\} \times \exp\left(-\frac{E_a}{RT_i}\right) \tag{1}$$

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

where $\mathrm{d}H_t/\mathrm{d}t$ is 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 ($\alpha = H_t/H_0$), T_0 the initial point at which DSC curve deviates from the baseline, R the gas constant, n the reaction order and E_a the apparent activation energy.

Taking logarithm of Eq. (1) , the following relation is obtained

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

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

$$\Omega = \sum_{i=1}^{m}\left\{\ln\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i - \ln\left\{AH_0(1-\alpha_i)^n\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\right\} + \frac{E_a}{RT_i}\right\}^2 \tag{3}$$

Eq. (3) is satisfied under condition that

$$\frac{\partial\Omega}{\partial A} = 0 \tag{4}$$

$$\frac{\partial\Omega}{\partial n} = 0 \tag{5}$$

$$\frac{\partial\Omega}{\partial E_a} = 0 \tag{6}$$

$$m\ln A + an = b + \frac{E_a}{R}c - m\ln H_0 - d \tag{7}$$

$$a\ln A + en = f + \frac{E_a}{R}g - a\ln H_0 - h \tag{8}$$

$$p - (\ln A + \ln H_0)g - nr - s + \frac{E_a}{R}W = 0 \tag{9}$$

where

$$a = \sum_{i=1}^{m}\ln(1-\alpha_i) \tag{10}$$

$$b = \sum_{i=1}^{m}\ln\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i \tag{11}$$

$$c = \sum_{i=1}^{m}\frac{1}{T_i} \tag{12}$$

$$d = \sum_{i=1}^{m}\ln\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right] \tag{13}$$

$$e = \sum_{i=1}^{m}\ln^2(1-\alpha_i) \tag{14}$$

$$f=\sum_{i=1}^{m}\ln\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i\ln(1-\alpha_i) \tag{15}$$

$$g=\sum_{i=1}^{m}\frac{\ln(1-\alpha_i)}{T_i} \tag{16}$$

$$h=\sum_{i=1}^{m}\left\{\ln\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\ln(1-\alpha_i)\right. \tag{17}$$

$$Q_i=\frac{1}{RT_i}-\frac{1-(T_0/T_i)}{RT_i+E_a(1-(T_0/T_i))} \tag{18}$$

$$p=\sum_{i=1}^{m}Q_i\ln\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i \tag{19}$$

$$q=\sum_{i=1}^{m}Q_i \tag{20}$$

$$r=\sum_{i=1}^{m}Q_i\ln(1-\alpha_i) \tag{21}$$

$$s=\sum_{i=1}^{m}Q_i\ln\left[1+\frac{E_a}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right] \tag{22}$$

$$W=\sum_{i=1}^{m}\frac{Q_i}{T_i} \tag{23}$$

Solving Eqs. (7) and (8) we obtain

$$\ln A=\frac{(b-d)e+(h-f)a+(E_a/R)(ce-ga)}{-(a^2-me)}-\ln H_0 \tag{24}$$

and

$$n=\frac{(b-d)a+(h-f)m+(E_a/R)(ac-gm)}{a^2-me} \tag{25}$$

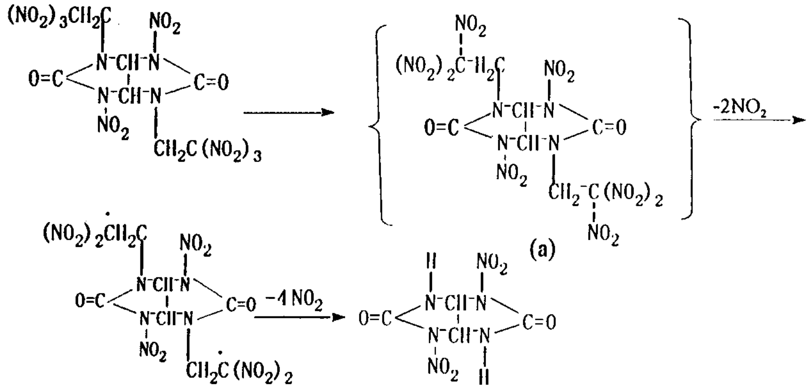
Table 2
Data of the title compound determined by DSC[a]

Data point	T_i (K)	α_i	$(\mathrm{d}H_i/\mathrm{d}t)_i$ (mJ s^{-1})
1	458.2	0.0268	0.1920
2	459.2	0.0536	0.2720
3	461.2	0.0848	0.3960
4	463.2	0.1384	0.4840
5	463.7	0.1920	0.5520
6	464.2	0.2188	0.5960
7	465.2	0.3214	0.7200

[a] $T_0 = 454.2$ K; $H_0 = 268.8$ mJ; $\beta = 2.14$ °C min^{-1}.

The values of p, $\ln A$, q, n, r, s and W in Eq. (9) are correlated with the value of E_a. Once the value of E_a has been calculated from Eq. (9), the corresponding values of A and n can be obtained from Eqs. (24) and (25).

By substituting the original data tabulated in Table 2 into above-mentioned Eqs. (10)–(23), the value of E_a of 203.1 kJ mol^{-1} is obtained by Eq. (9) and the values of A of $10^{19.9}$ s^{-1} and n of 0 are obtained by Eqs. (24) and (25), respectively. The values of E_a, A and n obtained by Eq. (2) with the iterative method [5] (program DM) on the computer are 201.7 kJ mol^{-1}, $10^{19.7}$ s^{-1} and 0, respectively. The linear correlation coefficient and standard mean square deviation are 0.9792 and 0.0236, respectively. 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. The value of E_a approached the dissociation energy of the C–NO_2 bond, indicating that the activated complex (a) as shown by the reaction mechanism in the abstract, could be formed during decomposition.



The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (26) taken from [6] is 182.3 °C.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1, ..., 5 \tag{26}$$

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (27) taken from [6] is 191.4 °C.

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O R T_{p0}}}{2R} \tag{27}$$

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 ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) corresponding to $T = T_{p0}$, $E = E_a$ and $A = A_k$ obtained by Eqs. (28)–(30) are 132.5 J mol^{-1} K^{-1}, 199.09 and 138.74 kJ mol^{-1}, respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^{\neq}/R} \tag{28}$$

$$A \exp\left(-\frac{E_a}{RT}\right) = \left(\frac{k_B T}{h}\right) \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{29}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{30}$$

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

4. Conclusions

The mechanism of the exothermic first-stage decomposition reaction for the title compound could be expressed by the reaction mechanism shown in the abstract. The apparent activation energy, pre-exponential constant and reaction order of this reaction are 203.1 kJ mol^{-1}, $10^{19.9}$ s^{-1} and 0, respectively. The critical temperature of thermal explosion of the compound is 191.4 °C. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of the reaction at T_{p0} are 132.5 J mol^{-1}, 199.09 and 138.74 kJ mol^{-1}, respectively.

References

[1] F. Yingao, W. Guohua, Hanneng Cailiao 5 (1) (1997) 9–14.

[2] H. Rongzu, L. Yanjun, F. Yingao, W. Jinsheng, X. Yi, J. Therm. Anal. 46 (1996) 283–1289.

[3] H.E. Kissinger, Anal. Chem. 29 (1957) 1702–1706.

[4] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881–1886.

[5] H. Rongzu, Y. Zhengquan, L. Yanjun, Thermochim. Acta 123 (1988) 135–151.

[6] Z. Tonglai, H. Rongzu, X. Yi, L. Fuping, Thermochim. Acta 244 (1994) 171–176.